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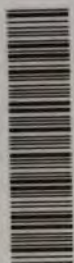
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SCHEME FOR THE DETECTION OF THE
MORE COMMON CLASSES
OF
CARBON COMPOUNDS

FRANK E. WESTON

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CARBON COMPOUNDS

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A SCHEME FOR THE DETECTION OF THE
MORE COMMON CLASSES
OF
CARBON COMPOUNDS

BY

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THIRD EDITION

LONGMANS, GREEN, AND CO.

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1912

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P R E F A C E

THE lack of any systematic scheme for the identification of carbon compounds suitable for students preparing for the Final B.Sc. Examination of London and Honours Chemistry Examination of the Board of Education, led the Author to draw up the present notes—primarily for the use of his own students at the Polytechnic Institute, Regent Street, W.

This scheme, which has grown to its present form as the result of several years' experience, has been found so useful to his own and other students, that the Author ventures to offer it to a wider public. The scheme enables a student to assign a carbon compound to its class, and, in many cases, to identify the body completely. The reactions of the commonest substances are omitted, since they are to be found in the usual analytical organic text-books.

POLYTECHNIC INSTITUTE,
REGENT STREET, W.,
September, 1904.

P R E F A C E TO SECOND EDITION

IN the present edition details of some of the general reactions have been amplified, and recent work in this direction included.

In order to systematize the work of the beginner in the study of "Analytical Chemistry of the Carbon Compounds," the more important reactions of the compounds mentioned in the First and Second Stages of the Syllabus of the Board of Education—

PREFACE TO THIRD EDITION

the names of these compounds are printed in heavy type in the text—have been added; this will facilitate the complete identification of a compound after the class to which it belongs has been ascertained.

It is thus hoped that a more comprehensive view of the subject will be obtained by the beginner than from the indiscriminate testing of a few common compounds.

F. E. W.

August, 1907.

PREFACE TO THIRD EDITION

SEVERAL additions have been made in the present edition, chief of which may be noted the following:—the identification of aldehydes and ketones by the formation of their semi-carbazone derivatives and also the reactions by which the latter may be recognized; the identification of the sugars by the microscopic examination of their osazones, photomicrographs of which, taken in the Author's laboratory, are given as a guide; a quick method of determining the densities of small quantities of liquid substances, a determination which will assist in identifying a body completely in those cases where, after ascertaining the class to which the compound belongs, no qualitative test is available to attain that end.

Where systematic practical work is taken in conjunction with lecture work the present edition will be found to be of as great use to the beginner as to the more advanced student.

F. E. W.

June, 1912.

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CARBON COMPOUNDS

PRELIMINARY OBSERVATIONS.

- I. Note carefully the obvious properties of substance, and determine m.p. or b.p. of it to ascertain if a single substance.

1. *Siwoloboff's*¹ *method of determining b.p.* (see Fig. 1).

Prepare a capillary tube 3 cms. $\times$ 1 mm. with a constriction 1 cm. from one end. Place this in a small test-tube 5 cms. $\times$ 0.5 cm. with enough of the liquid to cover the shorter tube. Fasten this test-tube to a thermometer so that liquid in it is next to the bulb of the thermometer. Fix up the thermometer to dip into heating bath—water if b.p. below 100°; conc. H_2SO_4 if above 100° C. and up to 200° C. On heating the bath, bubbles of gas will be seen to escape from lower open end of capillary slowly and irregularly, but when the liquid under examination attains the temperature

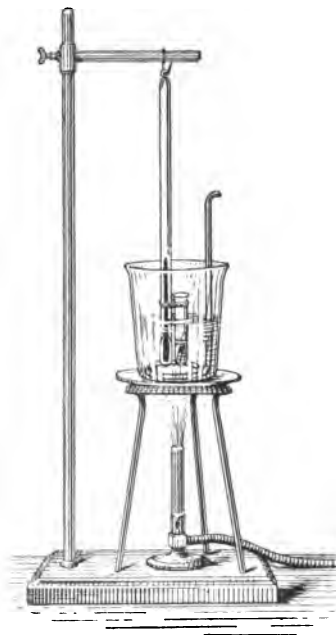


FIG. 1.

¹ Ber. 19, 795.

of its b.p., a continuous and regular succession of bubbles of gas will be obtained. Two or three observations should be made, but the small capillary should be taken out of the test-tube and replaced between two successive observations. The essential points of the determination are (i.) the bath must be well stirred during the determination, and (ii.) the b.p. is that temperature at which, on allowing the bath to cool after a rapid evolution of bubbles has been observed from the capillary tube, no bubble is seen to escape from the capillary, and no liquid to enter the capillary.¹

2. *Determination of melting point.*

Method 1.—Where only a small quantity of the solid is available, a little of the well-dried substance is placed in a small capillary tube closed at one end (see Fig. 2); the capillary tube is fastened to the stem of a thermometer so that the substance is opposite the bulb of the latter. The thermometer is then suspended in a suitable bath, which is heated and *constantly stirred* so that the rise in temperature is gradual. The temperature of melting is that at which the solid becomes transparent. The bath is allowed to cool a few degrees below the observed m.p. and the operation again repeated. (See Fig. 3.)

Method 2.—Where several grams of the substance are available, and it has been found by heating a small quantity in a small test-tube that no decomposition occurs on melting, enough of the substance is taken in a test-tube 7 cms. $\times$ 1.5 cms. to well cover the bulb of the thermometer when the latter is immersed in the substance. The test-tube is suspended in a suitable bath, whose temperature is gradually raised with stirring, and the temperature of the thermometer noted. The substance is stirred with the thermometer, and the m.p. is that temperature at which the thermometer remains stationary whilst the substance is changing its state from solid to liquid. On withdrawing the test-tube and allowing it to cool, it will be observed that the mercury in the thermometer remains stationary whilst the liquid is solidifying. Repeat the two operations. (See Fig. 4.)

II. Test very carefully for the elements N, Cl, Br, I, P, and S. (H should also be tested for, since CCl_4 contains none.)

¹ See *Trans. Faraday Society*, vol. iv. pt. 2, p. 95.

(a) *Beilstein's test for the halogens.*

Heat a small piece of CuO , held in a platinum wire, in the bunsen flame till no coloration of the flame is produced ; cool and dip the piece of CuO into the substance under examination if liquid (in case of solid, warm the CuO till a little of solid adheres to it), and then heat in the bunsen flame again ; a green coloration of the flame indicates the presence of a halogen. Lassaigne's test will distinguish between the halogens.



FIG. 2.

(b) *Sodium reaction for detecting N, S, and halogens (Lassaigne's test).*

Prepare a hard glass test-tube 10 cms. $\times$ 1 cm., and support it vertically from a piece of asbestos cardboard, 5×5 cms., resting on the ring of a retort stand (Fig. 5). Drop a piece of clean Na into the test-tube, and carefully heat it till it melts and begins to vaporize ; then drop into the test-tube about 0.1 gram of the substance, so that it falls directly on to the Na—if a liquid, use a dropping-tube, and allow to fall drop by drop without touching sides of tube. Continue to heat the tube strongly till all apparent change is over. Allow tube to cool, and then add 1 to 2 c.c. of alcohol to dissolve excess of Na.¹

NOTE.—Unless particular attention is paid to the initial stage of this test, namely, the making certain that the substance is acted upon by the Na and does not volatilize or sublime before this can take place ; and secondly, that heat is continued till all apparent change is over, many compounds containing N will fail to show the presence of it.

When effervescence due to Na is over, add 10 c.c. of boiling water, boil 2 or 3 minutes, filter ; repeat with 10 c.c. more boiling water, filter, and collect with first filtrate. Examine filtrate as below—

- (i.) To 10 c.c. add 5 c.c. of saturated solution of FeSO_4 , and few drops of NaOH soln. ; well boil ; add 2 or 3 drops

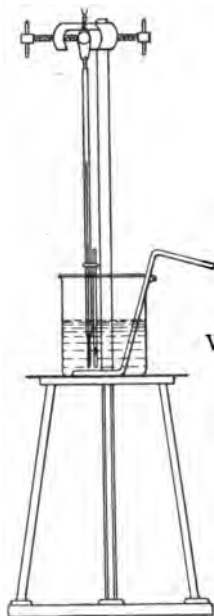


FIG. 3.

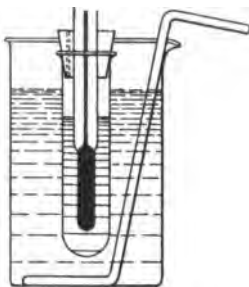


FIG. 4.

¹ Ordinary $5 \times \frac{1}{8}$ in. test-tubes may be used for this test, but they will be destroyed at each test. The hot test-tube may be plunged directly into an evaporating basin half filled with water, taking care that any unused Na is not projected on to the hands, etc., well boiled, etc., etc.

of FeCl_3 , cool, and make solution acid by carefully adding conc. HCl . A blue solution or precipitate shows formation of Prussian blue, and hence presence of a cyanide, and therefore presence of N in original substance.¹ (N.B.—If a greenish solution, or greenish-blue solution, is obtained, repeat ignition with Na, taking care that substance actually comes in contact with melted Na, and is well heated.)

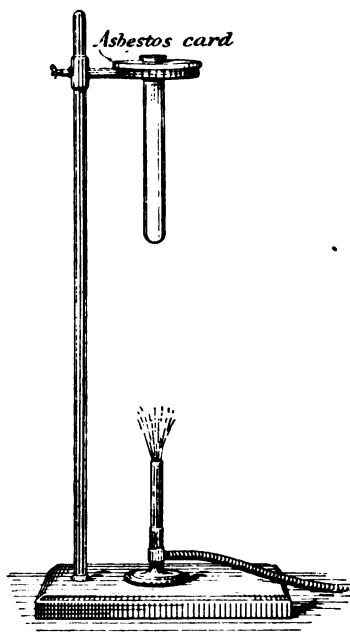


FIG. 5.

- (ii.) (a) Acidify 5 c.c. of filtrate with HNO_3 , and well boil (to expel HCN if present), and add AgNO_3 soln., a curdy white, or whitish-yellow ppt. = AgCl , AgBr , or AgI . By usual tests ascertain which. Hence presence of Cl , Br , or I .

¹ The N may be present in any of the forms in which it exists in carbon compounds.

- (b) Acidify 5 c.c. of filtrate with HNO_3 , well boil, add NH_4OH (till alkaline) and then add AgNO_3 soln., a deep yellow ppt. insol. in NH_4OH , but soluble in HNO_3 , is silver cyanamide Ag_2CN_2 . Hence presence of N.¹
- (iii.) To 2 c.c. of filtrate add a freshly prepared solution of sodium nitro-prusside. A violet coloration shows presence of a sulphide, and hence S in original substance. Confirm by soln. of $(\text{CH}_3\text{COO})_2\text{Pb}$ in original solution.
- (iv.) To 2 c.c. of filtrate neutralized by HCl add a few drops of FeCl_3 soln. A deep red coloration discharged by a soln. of HgCl_2 shows presence of a sulphocyanide, and hence of S and N in original substance.

(b') *Castellana's test for Nitrogen.*²

An intimate mixture of *well-dried* K_2CO_3 and Mg powder is made in the proportion of 2 parts K_2CO_3 to 1 part Mg powder.

Heat 0.2 to 0.3 gram of this mixture in a test-tube till action commences, and then drop into the reacting mixture 0.05 to 0.1 gram of the substance under test : continue heating till all action over, plunge the test-tube into cold water in a basin, acidify with HCl and boil, filter if necessary, and test for cyanide as in Lassaigne's test. Halogens can also be tested for if HNO_3 is used instead of HCl . Sulphur also can be tested for as in Lassaigne's test.

(c) *Test for P.*

Melt a mixture of 1 gram K_2CO_3 and 1 gram KNO_3 in a porcelain crucible ; carefully drop in 0.1 to 0.2 gram of substance, and continue heating till effervescence ceases. Boil with 10 c.c. water, filter, acidify with conc. HNO_3 , drop by drop, and test this solution for H_3PO_4 by $(\text{NH}_4)_2\text{MoO}_4$.

¹ Many compounds, viz. urea, urethane, and compounds of a similar type, produce cyanamide on treating with Na, and hence need of above test.

² *Gazetta*, 1904, 34, ii. 357-360.

NOTE.—H. R. Ellis (See *Chem. News*, vol. cii., No. 2655) criticizes the test and states that if the mixture of Mg and K_2CO_3 be heated slowly without largely exposing to the air, cyanide is formed, without adding any nitrogen compound ; if violently heated with plenty of air, no cyanide is formed under the same conditions. Ellis also states that urea, nitrophenols, nitro-compounds, and picric acid readily yield cyanide under this test, which they do not do under Lassaigne's test.

NOTE.—(i.) AgNO_3 gives a white ppt. of AgCNS from HNO_3 solutions of sulphocyanides, hence if latter present chlorides must be confirmed in (b) (i.) by digesting ppt. with very dilute AmOH , filtering and acidifying filtrate with HNO_3 , when white ppt. = AgCl .

(ii.) Phosphates of organic bases, without fusion, give the reaction for phosphoric acid with ammonium molybdate.

Oxygen cannot be tested for by any direct test. Its presence or absence will be indicated indirectly by some of the following observations :—

III. Burn a little of the substance on a roll of fine copper gauze (1 sq. cm. of gauze rolled upon the end of a stout piece of wire).

Aromatic compounds, hydrocarbons, unsaturated fatty compounds, and fatty compounds containing more than 4 C atoms produce soot.

IV. Ignite a portion (if solid) on Pt foil, and test residue, if any, for carbonate, sulphate, sulphite, oxide, or metal, which indicate—

(i.) Presence of a salt of—

(a) an organic acid.

(b) a sulphonic acid.

(c) an alkyl sulphate.

(d) a chloro-, bromo-, iodo-, nitro-, or amino-substituted acid.

(ii.) Presence of a metallic derivative of—

(a) a bisulphite of an aldehyde, or ketone.

(b) an amide.

(c) a mercaptan.

(d) a sulphonate, etc.

(e) a nitro compd., etc.

NOTE.—Carefully observe odour in III. and IV.

V. Try action of following on the substance :—

1. WATER.—A. If soluble test soln. with litmus (see Table of Solubilities). If solution obtained, to it add soln. of KOH till alkaline ; a ppt. may be—

- (i.) Metallic hydrate from a metallic derivative (see IV.).
 - (ii.) An organic base liberated from a salt of (a) An Amine, *e.g.* CH_3NH_2 , from its salts as a gas soluble in water, having a strong ammoniacal smell; $(\text{CH}_3)_3\text{N}$, from its salts, soluble in water, having a penetrating, fish-like, ammoniacal smell; $\text{C}_6\text{H}_5\text{NH}_2$ separates from solutions of its salts as an oil with characteristic odour: (b) An Alkaloid; morphine is precipitated from solns. of its salts, soluble in excess of KOH soln.
 - (iii.) Chloroform is liberated from solutions of chloral hydrate, especially on warming, giving an oily emulsion and characteristic odour.
 - (iv.) Of esters, methyl oxalate is easily soluble in water, producing an acid solution.
- B. Acid halides evolve halogen acids (aromatic may require warming) as dense white fumes. The substance may or may not dissolve in the water, depending upon whether the acid produced is soluble or not in water.

2. COLD KOH SOLN.

- (i.) NH_3 evolved from ammonium salts and detected on warming. (Aldehyde ammonia, m.p. 70° – 80° , evolves NH_3 .)
- (ii.) Amines liberated from their salts and detected by smell and alkalinity—more so on warming (see V. 1. (ii)).
- (iii.) Acids, phenols (also halogen and nitro derivatives), and most amides dissolve (sulphonamides dissolve). Nitrophenols produce yellow to red solutions.
- (iv.) Some esters may dissolve—more easily on heating.
- (v.) Chloral and chloral hydrate evolve CHCl_3 , detected by odour on warming.

3. COLD CONC. H_2SO_4 .

- (i.) Saturated and aromatic hydrocarbons and their halogen derivatives insoluble.
- (ii.) All other substances dissolve or are destroyed excepting a few acids and N compounds.
- (iii.) Deep red coloration indicates certain glucosides, *e.g.* salicine, amygdalin, etc.

3a. HOT CONC. H_2SO_4 . Gently warm about 0.2 gram with 1 c.c. of conc. H_2SO_4 .

- (i.) Blackening with effervescence of CO_2 , SO_2 , and CO (one or more of these)—
 - (a) Carbohydrates and certain glucosides, *e.g.* cane sugar, starch, etc.
 - (b) Alkaloids.
 - (c) Certain higher oxyacids, *e.g.* tartaric, citric, lactic and (oleic), and their salts.
- (ii.) Blackening without effervescence—
 - (a) Certain poly-phenols, *e.g.* pyrogalllic acid.
 - (b) „ phenol acids, *e.g.* salicylic, gallic, tannic, meconic acids and their salts.
- (iii.) Effervescence and no blackening—
 - (a) Certain acids, *e.g.* formic (CO evolved), oxalic (CO and CO_2 evolved), citric (CO, CO_2 , and SO_2 evolved), and their salts.
 - (b) Certain nitrogen compounds, *e.g.* HCN evolved from cyanides, ferrocyanides, ferricyanides, and sulphocyanides.
- (iv.) Pungent vapour evolved without effervescence and blackening—
 - (a) Certain acids, *e.g.* acetic, benzoic, succinic, and their salts.
 - (b) Certain phenols, *e.g.* phenol and its metallic derivations.

4. **SODA LIME.** Intimately mix 0.2 gram substance with 5 grams of well-dried powdered soda-lime ; place mixture in hard glass test-tube, and then 2 grams of coarsely grained soda-lime ; fit cork, and short right-angled tube. Strongly heat coarse soda-lime and then the mixture (Fig. 6).

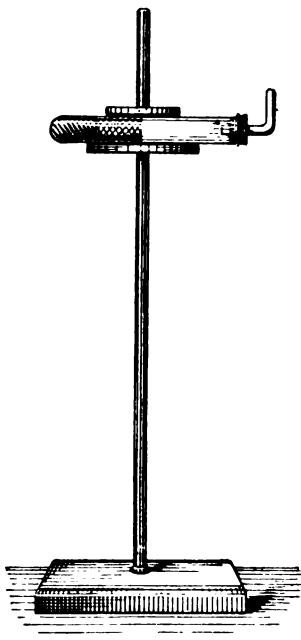


FIG. 6.

(i.) NH_3 gas or ammoniacal vapours evolved from (smell and litmus paper)—

- (a) Ammonium salts.
- (b) Ammonium derivatives—Amines, *e.g.* methyl-amine salts, ethylamine salts. methyl-ammonium salts ; Amides, *e.g.* oxamide ; Ureas, Uræides, Uric acid and

derivatives; Cyanides,¹ *e.g.* ferrocyanides, ferricyanides; Alkaloids,¹ etc.

(ii.) Inflammable gas evolved—

(a) H from formates, oxalates.

²(b) Hydrocarbons from acids or salts (C_6H_6 from all aromatic acids with COOH group attached to benzene nucleus).

²(iii.) Phenols produced from Oxy-aromatic acids or salts, *e.g.* salicylic acid and salts.

(iv.) Smell of burnt sugar from—

(a) Carbohydrates, *e.g.* sugars, starch.

(b) Glucosides.

(c) Certain higher acids, *e.g.* citric, tartaric, malic, tannic, gallic, and their salts.

5. Na_2CO_3 SOLN. Add 0.1 to 0.2 gram of substance to 10 c.c. of 10% Na_2CO_3 soln.

(i.) Acids dissolve, but monohydric phenols insoluble.

(ii.) Chlorophenols and nitrophenols dissolve.

(iii.) Polyhydric phenols dissolve.

NOTE.—This test only applies when the substance is insoluble in water.

6. METALLIC Na.—A. Dissolve substance³ (or suspend) in anhydrous alcohol free ether, and add a clean thin slice of Na 1×0.5 cm.

The apparatus shown in Fig. 7 will be found useful for carrying out this test.

¹ These compounds produce an unpleasant smell of burning animal matter or singed flesh in this reaction.

² By taking from 2 to 5 grams of the substance and fixing a small condenser to ignition tube, sufficient hydrocarbon or phenol may be obtained to enable a b.p. or m.p. determination to be made after purifying and drying.

³ If substance is a liquid, it should be perfectly dry before applying this test; also no solvent need be used. The liquid may be dried by standing 1 to 2 c.c. of it in a corked test-tube with (1) a few pieces of fused $CaCl_2$, (2) 1 or 2 grams of K_2CO_3 , or (3) 1 or 2 grams of anhydrous $CaSO_4$.

a is a small test-tube 7.5 cms. $\times$ 1 cm., into which the ethereal soln. and Na are placed.

b and *c* are test-tubes 12.5 $\times$ 2.5 cms. ; *b* is filled with water. The connecting tubes are made of small-bore tubing.

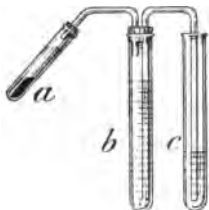


FIG. 7.



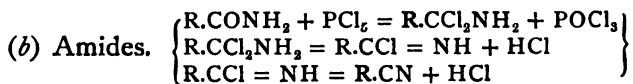
FIG. 8.

The gas evolved in *a* is collected in *b*, and water expelled in *c*. When action is over, the water in *b* and *c* can be levelled, and tube *a* disconnected. The gas in *b* can then be collected in test-tubes over a basin of water by pouring water into *c* (Fig. 8).

- (i.) H is evolved from :—Compounds containing OH group, *e.g.* [Alcohols, phenols, acids], aldehydes, ketones, esters, amides, mercaptans, and hydrazines.
- (ii.) Hydrocarbons evolved from halides of the lower hydrocarbons, *e.g.* C_4H_{10} from C_2H_5I and C_2H_5Br .

B. If H evolved, or if OH group suspected, but no H evolved, mix about 0.1 gram of the dry substance in a dry test-tube with 0.2 to 0.3 gram PCl_5 (if no action, gently warm). HCl gas will be evolved from compounds containing—

- (a) OH group, viz. acids, alcohols, phenols, etc., *e.g.*—
 - (a) Methyl and ethyl alcohol; allyl alcohol; glycerol; phenol, etc.
 - (b) Formic, acetic, oxalic, palmitic, tartaric, succinic, benzoic and salicylic acids, etc.
 - (c) Cane sugar, dextrose, lactose, and starch, etc.



e.g. acetamide, oxamide, benzamide, etc.

C. Confirm the presence of OH or NH₂ group by the action of (i.) CH₃COCl, and (ii.) C₆H₅COCl (see IX. C. 2).

7. Br IN CCl₄.¹ Dissolve substance in CCl₄, or in some solvent² having no action on Br, and add to it drop by drop a soln. of Br in CCl₄.

(i.) Decolorized instantly without evolution of HBr shows double or treble linking (including Terpenes).

(ii.) Decolorized with evolution of HBr shows substitution.

NOTE.—

(a) Phenols, amines, aldehydes, and ketones decolorize instantly.

(b) Some amines do so without evolution of HBr.

(c) A ppt. may be obtained on adding Br. This may be due to—

(a) Certain mono-, di-, and trihydric phenols.

(β) Certain oxy-aromatic acids and aromatic amines.

(γ) Certain alkaloids.

N.B.—Br water may be added to a water soln. of the substance to see if decolorization takes place, but the evolution of HBr will not be observed owing to its solubility in water.

8. KMnO₄ SOLN (von Baeyer's test). To 0.1 gram substance in 5 c.c. of 5% soln. of Na₂CO₃ add drop by drop a 1% soln. KMnO₄.

¹ If substance is a liquid, add the Br in CCl₄ directly to it.

² *e.g.* Ligroine, petroleum ether, carbon bisulphide, chloroform.

(i.) Unsaturated bodies decolorize it.

(ii.) Saturated do not.

EXCEPTIONS.—Following bodies are oxidized, and hence decolorize it: Formic acid, malonic ether, phenols, nitrophenols, etc., oxybenzoic acids, aldehyde bisulphite, acetone, benzaldehyde, nitrobenzaldehyde, etc., acetophenone, glycerine, and some sugars.

The further examination of the substance will depend upon (1) The elements found in the substance. (2) The solubility of it in water, KOH soln., and Na_2CO_3 soln. (3) The remaining properties discovered by preceding tests. The following tests are grouped under the headings of elements found.

If C and H only have been detected, and the substance is soluble in water, it may be taken for granted that O is present, since all hydrocarbons are insoluble in water. Similarly, presence of C, H, and a halogen easily soluble in water, indicates presence of O. If C and H only detected and insoluble in water, then not only should C and H compds. be tested for, but also insoluble C, H, and O compds.

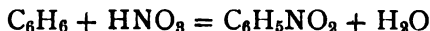
VI. CARBON AND HYDROGEN ONLY PRESENT.

Tests V. 3, 7, and 8 will have detected saturated or unsaturated body. To further differentiate—

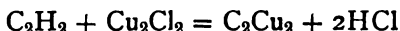
1. Carefully mix 0.5 c.c. or 0.5 gram of substance with 5 c.c. fuming H_2SO_4 , stand for 5 minutes, gently warm for 2 or 3 minutes, carefully pour into 20 c.c. of cold water, and allow to stand. If entirely dissolved most probably aromatic, *e.g.*



2. Repeat 1, using fuming HNO_3 instead of H_2SO_4 (take very great care). Aromatic compounds form insoluble nitro-compounds which can be separated, washed, dried, and tested for N (see Lassaigne's test for N), *e.g.*



3. To 0.5 c.c. or 0.5 gram of dry substance add 0.5 gram of anhydrous AlCl_3 , and then add 0.5 c.c. of dry CHCl_3 , drop by drop; an evolution of HCl gas is produced if hydrocarbon is aromatic (Friedel and Craft's reaction) —[if no action in cold, gently warm].
4. To detect triple bond: To 5 c.c. of an ammoniacal soln. of Cu_2Cl_2 add from 0.5 to 1 c.c. of the substance (if liquid), shake, and allow to settle; a coloured precipitate (red, green, or yellow) indicates a double compound of a hydrocarbon, containing a triple bond, with Cu_2Cl_2 , *e.g.*



5. Terpenes may be distinguished by the formation of solid bromides or hydrochloride, *e.g.*
 - (i.) Dissolve 1 c.c. of compound in 4 c.c. of alcohol and 4 c.c. of ether; cool with ice, and add 1 c.c. of Br ; a solid di- or tetra-bromide settles out which may be recrystallized from ether and m.p. determined.
 - (ii.) Dissolve 1 c.c. of compound in 10 c.c. glacial acetic acid, and add Br as long as reaction takes place: recrystallize as in (i.).
 - (iii.) Pass dry HCl gas into 2 c.c. of the well-cooled liquid; a mono-hydrochloride is formed in some cases which can be recrystallized from alcohol or ether and m.p. determined.
 - (iv.) If moist HCl gas be used solid di-hydrochlorides are formed, which may be recrystallized as in (ii.).
6. To distinguish between various benzene hydrocarbons: heat 1 to 2 grams of substance under reflux with either dil. HNO_3 or glacial acetic solution of chromic acid, cool and filter.
[For oxidation use the following :—

- (1) HNO_3 —1 vol. acid to 3 vols. of water (requires long time).
- (2) CrO_3 —2 parts $\text{K}_2\text{Cr}_2\text{O}_7$, 3 parts conc. H_2SO_4 , and 2 to 3 parts H_2O .]

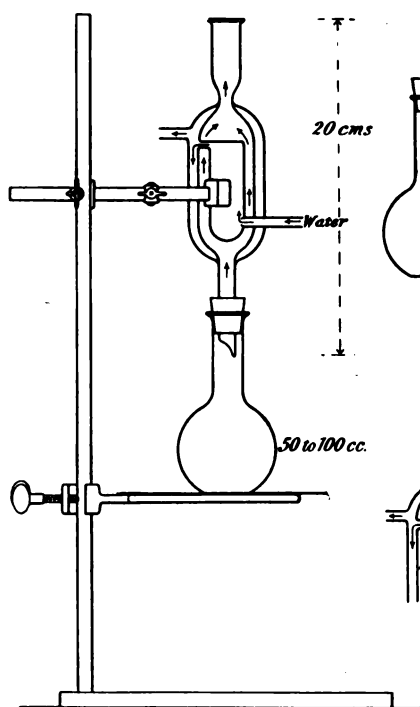


FIG. 9.

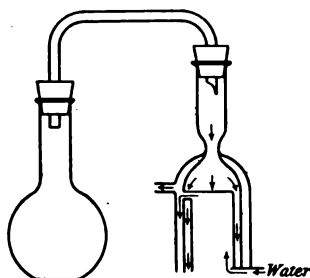


FIG. 10.

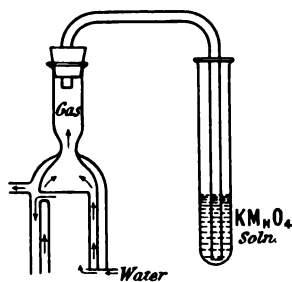


FIG. 11.

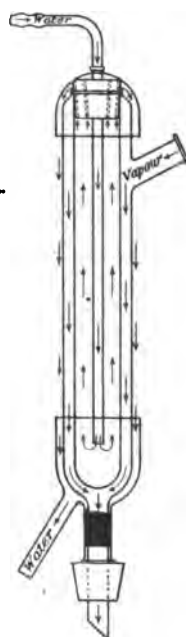


FIG. 11A.

- (1) For heating small quantities under a reflux, the apparatus depicted in the diagram (Fig. 9) will be found to meet all the cases occurring in this scheme.
- (2) By having another cork fitted with an adapter, the apparatus can readily be changed for distillation (see Fig. 10).
- (3) In some experiments with reflux, gases will be evolved ; these may be collected by fitting a small

delivery tube to condenser, and passing into a test-tube containing suitable reagents (see Fig. 11).

NOTE.—The condensers depicted belong to the double condensing surface type, and possess very small dead space where gases are to be collected (Fig. 11A).

Test residue for

- (i.) Benzoic acid :—from monosubstituted benzene (see IX. A. c.).
- (ii.) Phthalic acids :—
 - (a) Ortho—from o. disubstituted benzenes or naphthalene (with dilute HNO_3) ; sol. in hot water, alcohol, and ether. BaCl_2 gives a white ppt. to soln. of acid in NH_4OH . Fluorescent test with resorcin (see IX. 2 (4)).
 - (b) Iso—from m. disubstituted benzenes ; BaCl_2 gives no ppt. to soln. of acid in NH_4OH .
 - (c) Tere—from p. disubstituted benzenes ; almost insoluble in H_2O , alcohol, and ether ; BaCl_2 gives white ppt. with soln. of acid in NH_4OH .
- (iii.) Anthraquinone from anthracene ; anthraquinone may be identified as follows: Add 1 gram of anthraquinone to 5 c.c. of NaOH soln., then add 1 gram Zn dust and warm: a blood-red coloration is produced, due to the formation of oxanthranol. On shaking up with air the soln. is decolorized.
- (iv.) Naphthaquinone from naphthalene (acetic acid soln. of CrO_3).

NOTE.—Solns. of naphthalene, anthracene, and phenanthrene in benzene or toluene mixed with soln. of picric acid, in benzene, deposit yellow, red, and yellow crystalline derivatives respectively on evaporation.

The following are the more important hydrocarbons with their chief characteristics :—

n-Pentane, b.p. 38° . Commercial n-pentane boils from 37° – 39° , and has S.G. 0.626 at 17° C.¹

Isopentane, b.p. 30° ; S.G. 0.638 at 14° C.

n-Hexane, b.p. 71.5° ; S.G. 0.663 (occurs in petrol).

n-Heptane, b.p. 99° ; S.G. 0.696 (occurs in ligroine).

n-Octane, b.p. 125° ; S.G. 0.718 (occurs in ligroine).

Amylene (ordinary), b.p. 25° – 40° , is a mixture of β isoamylene, pentane, γ and α amylene.

Benzene, C_6H_6 , b.p. 80.5° ; m.p. 5° C. (about); S.G. 0.874 at 20° . A mobile, colourless liquid, with characteristic odour, completely solidifies when placed in ice (use about 1 c.c. in a t.t.).

1. Easily soluble in ether, glacial acetic acid, and carbon bisulphide.
2. To a cool mixture of 2 c.c. conc. H_2SO_4 and 1 c.c. conc. HNO_3 , add 1 c.c. of benzene drop by drop, keeping temperature below 50° C. Allow to stand five minutes at 50° C., and then pour into 50 c.c. of cold water: an oily layer of nitrobenzene settles out (odour of oil of bitter almonds). To a few drops of this oil add 5 c.c. of HCl (1 vol. of acid to 2 vols. of water), and then Zn dust little at a time till odour of nitrobenzene has disappeared. Now add a strong soln. of NaOH till pptd. $Zn(OH)_2$ is just dissolved; aniline will now be liberated, which can be separated with ether and identified by odour and carbylamine reaction, which see X. B. 3 (1).

Toluene, C_7H_8 , b.p. 110.3° . Yields C_6H_5COOH with either dil. HNO_3 or CrO_3 . S.G. 0.871 at 15° .

o-Xylene, C_8H_{10} , b.p. 141° – 142° . Yields o. $C_6H_4(COOH)_2$ with alk. $KMnO_4$ only. S.G. 0.890.

m-Xylene, C_8H_{10} , b.p. 137° . Yields iso- $C_6H_4(COOH)_2$ with alk. $KMnO_4$, and with dil. HNO_3 on long heating. S.G. 0.878 at 0° .

p-Xylene, C_8H_{10} , b.p. 136° – 137° . Yields tere- $C_6H_4(COOH)_2$ with CrO_3 easily, and with dil. HNO_3 on long heating. S.G. 0.862 at 19° ; $H_2SO_4 + HNO_3$ yield a tri-nitro derivative m.p. 137° .

Ethylbenzene, C_8H_{10} , b.p. 134° . Yields C_6H_5COOH with CrO_3 easily, and with dil. HNO_3 on long heating. S.G. 0.866 at 22° .

Mesitylene, (1,3,5-) C_9H_{12} , b.p. 163° . Yields trimesic acid $C_6H_3(COOH)_3$ easily with dil. HNO_3 . S.G. 0.870 at 20° . Cold $H_2SO_4 + HNO_3$ yield trinitro-compound m.p. 232° .

Cumene, $C_9H_8C_3H_7$ (iso), b.p. 153° . Yields C_6H_5COOH with dil. HNO_3 or CrO_3 . S.G. 0.879 at 0° .

Cymene, $C_6H_4 \begin{smallmatrix} CH_3 \\ \diagup \\ C_3H_7 \end{smallmatrix}$ ⁽¹⁾/₍₄₎, b.p. 175° – 176° . Yields tere- $C_6H_4(COOH)_2$ by dil. HNO_3 or CrO_3 . S.G. 0.8722 at 0° .

¹ See p. 19 for rapid method of determining S.G.

Hexamethyl benzene, $C_6(CH_3)_6$, b.p. 264° , m.p. 169° . Yields $C_6(CO_2H)_6$ by alk. $KMnO_4$.

Naphthalene, $C_{10}H_8$, m.p. 79° C. White crystalline mass or thin scales with characteristic odour.

1. Insoluble in cold water, sparingly soluble in petroleum ether, easily soluble in benzene and ether, and miscible in all proportions with hot toluene or absolute alcohol.
2. Add 0.5 gram of solid to 2.5 c.c. of conc. HNO_3 ; warm gently for 2 minutes and pour into water. Recrystallize the yellow α -nitronaphthalene from a small quantity of alcohol; dry and determine m.p. 61° C.
3. Make a saturated soln. of naphthalene in 2 c.c. benzene or toluene, and a similar soln. of picric acid; mix the two solutions; a fine golden-yellow ppt. of naphthalene picrate settles out. Filter and dry. Determine m.p. 149° . Naphthalene picrate = $C_{10}H_8 \cdot C_6H_2(NO_2)_3OH$.

Phenanthrene, $C_{14}H_{10}$, m.p. 99° . Yields $C_{14}H_8O_2$ (Phenanthraquinone) by CrO_3 , m.p. 198° . Phenanthrene picrate $C_{14}H_{10} \cdot C_6H_2(NO_2)_3OH$ yellow needles from alcoholic solution; m.p. 144° .

Anthracene, $C_{14}H_{10}$, m.p. 213° C. A white scaly crystalline solid, exhibiting a bluish-violet fluorescence when pure.

1. Insoluble in water; soluble, but not to any great extent, in ether, chloroform, carbon bisulphide, benzene, and toluene; less so in acetic acid.
2. Make a saturated soln. of anthracene in 5 c.c. of hot benzene, and add this soln. to 2 c.c. of a warm saturated soln. of picric acid in benzene; a red crys. ppt. of anthracene picrate settles out on cooling. Filter and dry, and determine m.p. 170° C. Anthracene picrate = $C_{14}H_{10} \cdot 2C_6H_2(NO_2)_3O$.
3. Dissolve 0.1 gram anthracene in 10 c.c. boiling glacial acetic acid contained in 100-c.c. flask fitted to a reflux; now add to boiling liquid, drop by drop, a soln. of 1 gram of chromic acid in 2 c.c. glacial acetic acid and 5 c.c. water. Boil for 5 minutes, and then pour contents of flask into 50 c.c. of water. Anthraquinone settles out as a yellow powder. Filter, wash, and dry. Determine m.p. 277° C.

Confirm the anthraquinone by conversion to oxanthranol test. (See VI. 6. iii.)

Styrolene (Cinnamene), $C_6H_5CH=CH_2$, b.p. 144° . Yields $C_6H_5CO_2H$ with CrO_3 ; S.G. 0.925 at 0° .

Phenylacetylene, $C_6H_5C \equiv CH$, b.p. 139° . Yields $C_6H_5CO_2H$ with CrO_3 ; yields $(C_6H_5)_2Cu_2$ bright yellow and $(C_6H_5)_2Ag_2$ white with ammoniacal Cu_2Cl_2 soln. and $AgNO_3$ soln. respectively.

Stilbene, $C_6H_5CH = CHC_6H_5$, m.p. 120° . Yields $C_6H_5CO_2H$ with CrO_3 or $KMnO_4$.

Isoprene, C_5H_8 , b.p. 37° .

Pinene, $C_{10}H_{16}$, b.p. 156° ; S.G. 0.858 at 20° , $[\alpha]_D \pm$, $C_{10}H_{16}HCl$, m.p. 125° , $C_{10}H_{16}Br_2$, m.p. 169° .

Limonene, $C_{10}H_{16}$, b.p. 176° ; S.G. 0.846 at 20° , $[\alpha]_D \pm 105^\circ$, $C_{10}H_{16}2HCl$, m.p. 50° , $C_{10}H_{16}Br_4$, m.p. 104° .

Sylvestrine, $C_{10}H_{16}$, b.p. 176° ; S.G. 0.847 at 20° , $[\alpha]_D + 66.3^\circ$, $C_{10}H_{16}2HCl$, m.p. 72° , $C_{10}H_{16}Br_4$, m.p. 135° .

Dipentene, $C_{10}H_{16}$, b.p. 178° ; S.G. 0.845 at 20° , $[\alpha]_D O$, $C_{10}H_{16}2HCl$, m.p. 50° , $C_{10}H_{16}Br_4$, m.p. 125° .

Terpinolene, $C_{10}H_{16}$, b.p. 185° – 189° , $[\alpha]_D O$, $C_{10}H_{16}2HCl$, m.p. 50° , $C_{10}H_{16}Br_4$, m.p. 116° .

Terpinene, $C_{10}H_{16}$, b.p. 180° ; S.G. 0.847 at 20° , $[\alpha]_D O$.

Phellandrene, $C_{10}H_{16}$, b.p. 170° ; S.G. 0.8558 at 10° , $[\alpha]_D \pm 1.76^\circ$.

Camphene, $C_{10}H_{16}$, m.p. 51° – 52° , $C_{10}H_{16}HCl$, m.p. 157° , $C_{10}H_{16}Br_2$, m.p. 90° .

Determination of Specific Gravity.—In many cases where a compound has been identified as far as the class to which it belongs, it is found difficult by qualitative means to identify the body completely. A determination of the S.G. of the substance, if a liquid, will often enable the body to be identified. The following simple piece of apparatus, known as "The University Pyknometer and Pipette," will enable this determination to be carried out quickly and accurately to 1 part in 1000 (see Fig. 12).

The small tube A drawn out to a fine capillary at each end is inserted in the tube by means of a ground-glass joint.

The tube A is withdrawn from B, cleaned, dried, and accurately weighed. It is then reinserted in B and placed with its lower end in pure distilled water, the indiarubber bulb C is gently pressed and then released, the water rises in A and overflows into B. When the bulb C has regained its normal form, A is drawn out of B—being held by its fine end—quickly dried with a piece of filter paper, and again weighed. This gives weight of water at a known temperature. The tube A is now filled with the required liquid and again weighed. The liquids used must be at a temperature not lower than that of the balance.

If it is required to determine the S.G. at a temperature lower than that of the balance, the tube A can be filled at the required temperature and weighed in a tared stoppered weighing bottle, when any liquid escaping is retained in the bottle.

The instrument is supplied with three tubes (A) of different volumes.¹

¹ The instrument is made by Muller, Orme & Co., Ltd., 148, High Holborn, W.C. Price 2s. 6d.

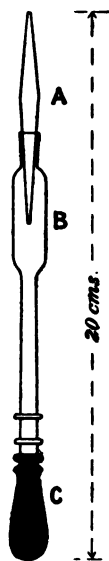


FIG. 12.

VII. CARBON, HYDROGEN, AND HALOGEN PRESENT.

Note odour carefully.

- (a) Pungent, irritating odour indicates alkyl aromatic compound with halogen in alkyl group.
 - (b) Aromatic odour indicates halogen in nucleus.
1. Digest 1 to 2 grams with 20 c.c. of alcoholic potash under reflux for 10 to 15 minutes.
 - (a) Observe whether any gas evolved, viz. C_2H_4 (from C_2H_5I or C_2H_5Br), C_3H_6 , C_4H_8 , or C_2H_2 . (Pass the gas into alkaline $KMnO_4$ solution. See Fig. 11.)
 - (b) Dilute residue in flask with water, filter, acidify with HNO_3 , and to a portion of soln. add $AgNO_3$:—ppt. = $AgCl$, $AgBr$, or AgI (identify which).

This reaction given by fatty derivatives or aromatic with halogen in side chain, but not by aromatic compounds with halogen in nucleus.

Methyl iodide, CH_3I , b.p. $42.3^\circ C.$; S.G. 2.285 at $15^\circ C.$

Ethyl Bromide, C_2H_5Br , b.p. 39° ; S.G. 1.47 at $13^\circ C.$ Colourless liquid, miscible in all proportions with alcohol and ether.

1. To 1 c.c. of dry benzene and 0.5 gram of anhydrous $AlCl_3$, add 2 or 3 drops of C_2H_5Br : white acid fumes of HBr evolved (Friedel and Craft's reaction).
2. Note evolution of C_2H_4 in 1 (a).

Ethyl Iodide, C_2H_5I , b.p. 72° ; S.G. 1.975 at $0^\circ C.$ Colourless, strongly refracting liquid with pleasant odour; miscible in all proportions with alcohol and ether.

1. Friedel and Craft's reaction gives HI .
2. To 5 c.c. of soln. of $AgNO_3$ add a few drops of C_2H_5I : greyish-black ppt. of metallic Ag produced.
3. To 0.5 c.c. of C_2H_5I add 1 c.c. of Br water and well shake: I is liberated, which can be identified in usual way.

Isopropyl bromide, C_3H_7Br , b.p. 60° – $63^\circ C.$; S.G. 1.309 at $20^\circ C.$

Isopropyl iodide, C_3H_7I , b.p. 89.9° ; S.G. 1.703 at $20^\circ C.$

Benzyl chloride, $C_6H_5CH_2Cl$, b.p. 176° ; S.G. 1.114 at 4° . Heated with a soln. of $Pb(NO_3)_2$ under reflux yields benzaldehyde (detected by odour of almonds).

Methylene chloride, CH_2Cl_2 , b.p. 42° ; S.G. 1.337.

Methylene bromide, CH_2Br_2 , b.p. 97° ; S.G. 2.498.

Methylene iodide, CH_2I_2 , b.p. 180° ; S.G. 3.292.

Ethylene chloride, $C_2H_4Cl_2$, b.p. 84° ; S.G. 1.260.

Ethylene bromide, $C_2H_4Br_2$, b.p. 131° ; S.G. 2.189.

Ethylidene chloride, CH_3CHCl_2 , b.p. 58° ; S.G. 1.189.

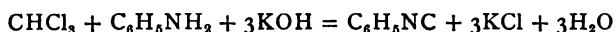
Benzal chloride, $C_6H_5CHCl_2$, b.p. 206° ; S.G. 1.295 at 16° . Heated with a soln. of $Pb(NO_3)_2$ in test-tube readily yields benzaldehyde.

Benzotrichloride, $C_6H_5CCl_3$, b.p. 213° ; S.G. 1.380 at 14° . Heated with water under reflux yields benzoic acid (which see for identification).

- (c) Test another portion of residue in flask for a
Formate : shows presence of $CHCl_3$ or $CHBr_3$.
 Test specially for $CHCl_3$, $CHBr_3$, CHI_3 , and CCl_4 .

Chloroform, $CHCl_3$, b.p. $61^\circ-62^\circ$ C.; S.G. 1.526 at 0° C. Colourless liquid with sweet agreeable ethereal odour; sparingly soluble in water, miscible with alcohol and ether.

1. To 5 c.c. of alcoholic KOH soln., add 2 or 3 drops of aniline and 1 to 2 drops of $CHCl_3$; gently warm : a disagreeable, characteristic odour of phenyl carbylamine evolved.



2. To 5 c.c. of Fehling's solution add 4 or 5 drops of $CHCl_3$, and well boil : a reddish ppt. of Cu_2O produced.



3. Dissolve 0.1 gram of α or β naphthol in 5 c.c. of conc. KOH and add a few drops of $CHCl_3$; on warming a fine blue liquid is obtained which changes on exposure to air to a green and brown liquid (Lustgarten).

Iodoform, CHI_3 , m.p. 119° C. A yellow crystalline solid with characteristic odour, soluble in alcohol and ether.

1. Friedel and Craft's reaction gives HI.
2. Mix 0.5 gram of CHI_3 with 3 grams of Zn dust; place in a hard glass test-tube and heat : C_2H_2 is evolved, which is identified by smell, burning, and effect on ammoniacal Cu_2Cl_2 soln.
3. Dissolve 0.2 gram phenol in 2 c.c. KOH soln.; to this soln. add 3

or 4 drops of a soln. of iodoform in alcohol and gently warm: a red ppt. is produced, which when dissolved in a small quantity of alcohol, produces a carmine-red soln. (Lustgarten).

Bromoform, CHBr_3 , b.p. 151°C . ; S.G. 2.904 at 15° and 2.83 at 0° .

Carbon Tetrachloride, CCl_4 , b.p. 77° . Colourless liquid. S.G. 1.608 at 10° .

1. Warmed with alc. KOH and few drops $\text{C}_6\text{H}_5\text{NH}_2$ gives odour of carbylamine after a few minutes.
 2. Treated with Zn and HCl reduced to CHCl_3 , which gives carbylamine reaction at once.
 3. Does not reduce Fehling's soln. ; CHCl_3 does on well boiling.
- Glyceryl chloride (Trichlorhydrin), $\text{C}_3\text{H}_5\text{Cl}_3$, b.p. 158° ; S.G. 1.417 at 15° .

2. Allyl derivatives identified by leek-like odour and tests V. 7 and 8.

Allyl chloride, $\text{C}_3\text{H}_5\text{Cl}$, b.p. 46° ; S.G. 0.9379 at 20° .

„ bromide, $\text{C}_3\text{H}_5\text{Br}$, b.p. 70° – 71°C . ; S.G. 1.461 at 0° .

„ iodide, $\text{C}_3\text{H}_5\text{I}$, b.p. 101°C . ; S.G. 1.798 at 16° .

3. Aromatic compounds with halogen in nucleus produce nitro-derivative easily, etc.

Chlor-benzene, $\text{C}_6\text{H}_5\text{Cl}$, b.p. 132°C . ; S.G. 1.128 at 0°C .

p. Dichlorobenzene, $\text{C}_6\text{H}_4\text{Cl}_2$, m.p. 56°C ., b.p. 173°C .

Brombenzene, $\text{C}_6\text{H}_5\text{Br}$, b.p. 155°C . ; S.G. 1.517 at 0°C .

p. Dibrom-benzene, $\text{C}_6\text{H}_4\text{Br}_2$, m.p. 89°C ., b.p. 218° .

Naphthalene Tetrachloride, $\text{C}_{10}\text{H}_8\text{Cl}_4$, m.p. 182°C . Colourless crystalline solid, soluble in ether and chloroform, sparingly in alcohol.

1. Treat 1 gram of naphthalene tetrachloride with 6 c.c. of conc. HNO_3 (S.G. 1.035) and evaporate carefully to dryness on sand-bath. Test residue for phthalic acid by the fluorescent test with resorcin (see IX., 2 (4)).

Monochlor-toluene, $\text{C}_6\text{H}_4\text{CH}_3\text{Cl}$; ortho. b.p. 156° ; para. m.p. 65° , b.p. 160°C .

Monobrom-toluene, $\text{C}_6\text{H}_4\text{CH}_3\text{Br}$; para. m.p. 28.5° , b.p. 185°C .

VIII. CARBON, HYDROGEN, OXYGEN, AND A HALOGEN PRESENT.

Indicates (a) Substituted Acids ; (b) Acid Halides ;
(c) Chloral and Chloral Hydrate.

Tests V. 1, 2, 5, and 6 will have indicated (a), (b), and (c).

1. SUBSTITUTED ACIDS.

- (1) Dissolve 0.5 to 1 gram in 50 c.c. N.NaOH soln., and titrate excess of alkali with $\frac{N}{10}$ H_2SO_4 , using phenolphthalein as indicator. Calculate from quantity of alkali used by substituted acid the equivalent weight of the acid.
- (2) Mix 0.5 gram of acid with 5 c.c. of water, and sufficient Na amalgam to make soln. alkaline when action over; filter; acidify filtrate with HCl, when organic acid is liberated from sodium salt. If acid insoluble, filter off; if soluble, extract with ether. Identify the acid as below (see "Detection of Acids"). In this reaction certain substituted acids are reduced to corresponding acids, viz.—
 - (i.) All substituted acetic acids;
 - (ii.) α dihalogen acids;
 - (iii.) $\alpha\beta$ dihalogen acids yield corresponding unsaturated acid.

Monochloroacetic Acid, $\text{CH}_2\text{Cl}.\text{CO}_2\text{H}$, m.p. 62°C ., b.p. $185^\circ\text{--}187^\circ\text{C}$. A white crystalline solid easily soluble in water.

- (1) Reduced with Na amalgam yields sodium acetate, which test for.

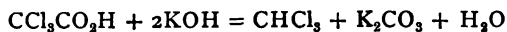
Dichloroacetic Acid, $\text{CHCl}_2.\text{CO}_2\text{H}$, b.p. 190° . Colourless liquid, easily soluble in water.

- (1) Reduced with Na amalgam yields sodium acetate, etc.
- (2) Neutralize 0.5 c.c. of the acid with NaOH soln.; add 1 c.c. AgNO_3 soln., and warm: a greyish-black deposit of metallic Ag obtained.
- (3) To 0.5 c.c. of acid add 10 % soln. of KOH till strongly alkaline and boil 5 minutes; test resulting soln. for potassium oxalate and potassium acetate.

Trichloroacetic Acid, $\text{CCl}_3.\text{CO}_2\text{H}$, m.p. 52°C ., b.p. 195°C . A white deliquescent crys. solid, easily soluble in water.

- (1) Reduced by Na amalgam to sodium acetate, etc.

- (2) Heat 0.5 gram of the acid with KOH soln. under reflux: chloroform and potassium carbonate produced. Test for chloroform.



Tribromacetic Acid, CBr_3COOH , m.p. 135°C . Crystalline solid, easily soluble in water.

Monochlorbenzoic Acid, $\text{C}_6\text{H}_4\text{Cl.CO}_2\text{H}$.

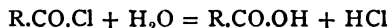
- (i.) ortho-, m.p. 137° . Crys. solid.
- (ii.) meta-, m.p. 153° . Crys. solid.
- (iii.) para-, m.p. 240° . Crys. solid.

Monobrombenzoic Acid, $\text{C}_6\text{H}_4\text{Br.CO}_2\text{H}$.

- (i.) ortho-, m.p. 147° . Crys. solid.
- (ii.) meta-, m.p. 155° . Crys. solid.
- (iii.) para-, m.p. 251° . Crys. solid, almost insoluble in water.

2. ACID HALIDES. (Easily soluble in ether, CS_2 , and C_6H_6 ; heavier than water.)

- (1) The free acid, from which derived, is obtained by decomposing with water. Carefully add 1 c.c. of acid to 5 c.c. of water; if no action, carefully heat; if no action, add NaOH and heat, when the sodium salt will be formed. Separate as 1 (2).



- (2) To 1 c.c. of absolute alcohol carefully add the acid halide drop by drop till action ceases; warm gently for 5 minutes, and pour into 10 c.c. of water. Separate the ester which settles out;¹ wash with dilute Na_2CO_3 , then water; dehydrate with fused CaCl_2 , and determine b.p. (Note also odour of ester.)

Acetyl Chloride $\text{CH}_3\text{CO.Cl}$, b.p. 55° . S.G. 1.130 at 0° .

„ Bromide $\text{CH}_3\text{CO.Br}$, b.p. 81° .

¹ If ester does not separate, add finely powdered NaCl to the soln. with shaking till no more dissolves; the ester then separates, and can be removed by means of separating funnel.

Propionyl Chloride $C_2H_5.CO.Cl$, b.p. 80° .

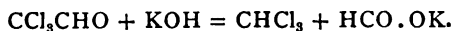
Benzoyl Chloride $C_6H_5.CO.Cl$, b.p. 197° .

„ Bromide $C_6H_5.CO.Br$, b.p. $217^\circ-220^\circ$.

3. If 1 and 2 absent, test specially for Chloral, or Chloral Hydrate.

Chloral, CCl_3CHO , b.p. $97^\circ C$. An oily, pungent-smelling liquid (somewhat like cucumber).

- (1) To 0.5 c.c. water add 2 or 3 drops of chloral ; a solid mass of chloral hydrate is produced.
- (2) To 5 c.c. of ammoniacal $AgNO_3$ soln. add soln. of 2 or 3 drops of chloral in 5 c.c. water ; metallic Ag is produced (a Ag mirror can be obtained if soln. is weak and test-tube clean).
- (3) Heat 0.5 c.c. chloral with 10 c.c. of 10 % KOH for 2 or 3 minutes : chloroform and potassium formate are produced, which test for.



- (4) Chloral gives the phenyl carbylamine reaction (see Chloroform).
- (5) To 10 c.c. of a very weak soln. of chloral in a t.t. add 1 drop of yellow Am_2S soln., so that it remains at top of solution ; boil the top layer of the soln., when a yellowish-white turbidity appears at the top and spreads downwards. Extremely weak soln. (1 in 4000) take 2 or 3 mins. for the colour to appear.

Chloral Hydrate, $CCl_3.C\begin{smallmatrix} OH \\ OH \end{smallmatrix}$, m.p. 57° . A white crystalline solid, having a characteristic odour (resembling cucumber), easily soluble in water.

- (1) To 0.5 gram chloral hydrate add 2 c.c. conc. H_2SO_4 and well shake : on allowing to stand chloral separates as a liquid on top of acid, and odour becomes stronger.
- (2) The characteristic reactions of chloral are given by chloral hydrate.

IX. CARBON, HYDROGEN, AND OXYGEN PRESENT.

Indicates Alcohols, Phenols (Phenol-alcohols, Phenol-aldehydes, etc.) ; Aldehydes, Ketones ; Ethers ;

Acids, Hydroxyacids, Aldehyde and Ketonic Acids, Acid Anhydrides ; Esters ; Carbohydrates ; Glucosides.

Tests V. 2, 4, 5, and 6 will have indicated acids and phenols. If indicated apply following :—

I. ACIDS OR SALTS.

(I) A systematic course should be gone through for the more common acids (see p. 37).

To obtain the acid from the salt, proceed as follows :

If soluble, carefully acidify with dil. HCl ; if insoluble, boil with Na_2CO_3 soln. ; filter ; carefully acidify filtrate with HCl. If acid is insoluble, it will be precipitated on acidifying, and can be filtered off. If acid is soluble, proceed as follows : Distil over $\frac{1}{3}$ of liquid, when acid will be in the distillate if volatile ; if acid not volatile, cool residue, and extract with ether, etc.

A. SATURATED ACIDS.

(a) Formic Acid, H.CO.OH. , b.p. 99° . Colourless liquid with pungent odour.

1. AgNO_3 soln. to soln. of acid or a formate gives white ppt. HCOOAg , turning to grey Ag on heating.
2. HgO dissolves in formic acid, and on heating gives white ppt. HCOOHg , with evolution of CO_2 and finally grey ppt. of Hg.
3. HgCl_2 soln. to soln. of acid or salt gives white ppt. of HCOOHg on heating, and finally grey ppt. of Hg.
4. FeCl_3 soln. added to neutral soln. of a formate produces red coloration discharged by HCl to yellow colour of FeCl_3 soln.
5. Test for free Formic Acid : To 5 c.c. of solution add 15 drops of conc. NaHSO_3 solution (1 : 1) ; shake and gently warm, when a reddish-yellow colour appears.¹

¹ E. Commanducci, *Gazetta*, 1906, 36, ii, 793. This reaction not given by formates : formaldehyde, acetaldehyde, crotonaldehyde, methyl or ethyl alcohol, glycerol ; acetic, butyric, valeric, lactic, oxalic, succinic, malic, tartaric, citric, benzoic, salicylic, and phthalic acids. The reaction is sensitive to 0.5 per cent. solution.

Acetic Acid, $\text{CH}_3\text{CO.OH}$, b.p. 118° , m.p. 16.6° .

Colourless liquid at ordinary temperature, with penetrating odour.

1. FeCl_3 soln. to neutral soln. of an acetate produces a red coloration, discharged by HCl to yellow colour of FeCl_3 soln.
2. AgNO_3 , HgO , and HgCl_2 are not reduced by solns. of acetates.
3. 5 c.c. of acetic acid or 1 gram of an acetate warmed with 1 c.c. abs. alcohol and 2 c.c. conc. H_2SO_4 yields ethyl acetate, which is recognized by characteristic fruity odour.
4. All acetates warmed with conc. H_2SO_4 evolve acetic acid, recognized by pungent odour.

Palmitic Acid, $\text{C}_{16}\text{H}_{31}\text{CO.OH}$, m.p. 62° . White crystalline solid, insol. in water, soluble in alcohol and ether. Determine equivalent by titration.

Propionic acid, $\text{C}_3\text{H}_5\text{CO.OH}$, b.p. 140° . Colourless liquid, miscible with water, alcohol, ether, and benzene. Fused CaCl_2 separates the acid from its aqueous soln.

Butyric acid, $\text{C}_4\text{H}_7\text{CO.OH}$, b.p. 155° ; S.G. 0.9587 at 20° . Colourless liquid with unpleasant smell, miscible with water.

- (1) Fused CaCl_2 separates the acid from its aqueous soln.
- (2) A cold saturated soln. of calcium butyrate precipitates the salt on boiling.
- (3) Copper acetate soln. added to conc. soln. of acid gives greenish-blue crys. ppt. of copper butyrate.

Iso-butyric acid, $(\text{CH}_3)_2\text{CH.COOH}$, b.p. 155° ; S.G. 0.949 at 20° . Unpleasant-smelling liquid.

Iso-valeric acid, $(\text{CH}_3)_2\text{CHCH}_2\text{CO.OH}$, b.p. 176° ;

S.G. 0.947. Liquid with powerful unpleasant smell, slightly soluble in water, miscible with alcohol and ether.

- (1) Fused CaCl_2 separates the acid from its aqueous soln.
- (2) Copper acetate soln. added to concentrated soln. of the acid gives oily drops of copper valerate, changing to greenish-blue powder.

Caproic acid (n), $\text{CH}_3(\text{CH}_2)_4\text{CO}_2\text{H}$. Oily liquid b.p. 205° ; S.G. 0.928 at 20° .

Capric acid, $\text{C}_9\text{H}_{19}\text{CO}_2\text{H}$, m.p. 31.4° . Its ethyl ester has fruity odour, and b.p. 243° .

Stearic acid, $\text{C}_{17}\text{H}_{35}\text{CO}_2\text{H}$, m.p. 62.2° . White pearly crys. plates; insol. in water, sol. in alcohol and ether.

(b) Oxalic Acid, $(\text{CO}_2\text{H})_2$, m.p. 101° of the hydrated crystalline solid. Soluble in water.

1. CaCl_2 soln. to neutral soln. of an oxalate gives white ppt. of CaC_2O_4 ; insol. in acetic acid, sol. in dilute HCl .
2. $\text{Ca}(\text{OH})_2$ soln. ditto.
3. Sols. of oxalates or oxalic acid warmed in presence of H_2SO_4 decolorize soln. of KMnO_4 when latter is added drop by drop.
4. Oxalates and oxalic acid heated with conc. H_2SO_4 evolve CO and CO_2 .

Succinic Acid, $\text{C}_2\text{H}_4(\text{CO}_2\text{H})_2$, m.p. 180° . White crys. solid, soluble in water.

1. Neutral FeCl_3 soln. to a neutral soln. of a succinate gives a dense reddish-brown ppt. of basic ferric succinate, easily soluble in HCl to a clear soln.
2. AgNO_3 soln. to neutral soln. of a succinate gives white ppt. of silver succinate unaltered in heating.
3. Succinic acid heated alone evolves irritating fumes which induce coughing.

4. Forms fluorescein dyes when heated with Resorcin and H_2SO_4 (see IX. 2 (4)).

Malonic acid, $\text{CH}_2(\text{CO.OH})_2$, m.p. 132° . White crys. solid, very soluble in water, alcohol, and ether.

1. To 0.01 gram of acid add 1 c.c. of acetic anhydride and heat: a reddish-yellow liquid with greenish-yellow fluorescence is produced (Kleeman, B. 19.2030).
2. Heat 0.2 gram in a dry test-tube; CO_2 and $\text{CH}_3\text{CO}_2\text{H}$ are evolved.
3. To 5 c.c. of cold neutral solution add CaCl_2 soln., calcium malate is pptd., soluble on heating.

(c) Benzoic Acid, $\text{C}_6\text{H}_5\text{CO.OH}$, m.p. 120° . White shining crys. needles or laminæ; difficultly soluble in cold water, readily in hot; soluble in alcohol and ether.

1. Neutral FeCl_3 soln. to a neutral soln. of a benzoate gives a flesh-coloured ppt. of basic ferric benzoate, soluble in HCl with the separation of white crys. ppt. of benzoic acid.
2. HCl added to a soln. of a benzoate gives a white crys. ppt. of benzoic acid.
3. Benzoic acid heated in dry tube melts and sublimes, giving off an aromatic-smelling vapour which induces coughing.

Phthalic acids, $\text{C}_6\text{H}_4(\text{COOH})_2$. See VI. (2) (ii.).

Phenylacetic acid, $\text{C}_6\text{H}_5\text{CH}_2.\text{CO.OH}$, m.p. 79.5° (oxidized to $\text{C}_6\text{H}_5\text{CO.OH}$ with CrO_3).

Hydrocinnamic acid, $\text{C}_6\text{H}_5\text{CH}_2.\text{CH}_2.\text{CO.OH}$, m.p. 47° (oxidized to $\text{C}_6\text{H}_5\text{CO.OH}$ with CrO_3).

Cumic acid, $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{C}_3\text{H}_7 \text{ (iso.)} \\ \text{CO.OH} \end{smallmatrix}$ 1, 4, m.p. 117° oxidized to terephthalic acid by CrO_3 . Distilled with lime, it yields cumene (isopropyl benzene).

Camphoric acid, $C_8H_{14}(CO_2H)_2$, m.p. 178° . Easily soluble in water.

(i.) Heated, loses water and gives anhydride, m.p. 217° , which sublimes in needles.

B. UNSATURATED ACIDS.

Test V. 7 will have indicated these. These may be identified by fusion with KOH, viz. Heat 1 gram solid KOH with 0.5 c.c. H_2O in a crucible till melted, then add about 0.5 gram of acid; carefully heat till effervescence ceases and mass nearly solidifies (do not char). Boil fused mass with 20 c.c. water, and filter. The filtrate contains the K salts of the acids formed during the fusion. These may be tested for—

Acrylic acid, b.p. 139° . $CH_2 = CH.CO_2H + 2KOH = HCO_2K + CH_3CO_2K + H_2$.

Crotonic acid, m.p. 72° . $CH_3.CH = CH.CO_2H + 2KOH = CH_3CO_2K + CH_3CO_2K + H_2$.

Angelica acid, m.p. 45° . $CH_3.CH \begin{smallmatrix} > \\ CH_3 \end{smallmatrix} C.CO_2H + 2KOH = CH_3.CO_2H + CH_3.CH_2CO_2K + H_2$.

Oleic acid, m.p. 14° . Yields palmitic and acetic acids.

Elaïdic acid, $C_{18}H_{34}O_2$, m.p. $44^\circ-45^\circ$. Yields $CH_3.CO_2H$ and $C_2H_5.CO_2H$.

Fumaric acid, $C_2H_2(CO_2H)_2$, sublimes at 200° . $C_2H_2(CO_2Ag)_2$ pptd. from neutral solns.

Maleic acid, $C_2H_2(CO_2H)_2$, m.p. 130° . Easily sol. in cold water.

Aconitic acid, $C_6H_5(CO_2H)_3$, m.p. $186^\circ-187^\circ$. Easily sol. in water, alcohol, and ether. Pb and Ca salts insol.

Cinnamic acid, m.p. 133° . $C_6H_5CH = CH.CO_2H + 2KOH = C_6H_5CO_2K + CH_3CO_2K + H_2$.

Atropic acid (α Phenylacrylic acid), m.p. 106° . (a) CrO_3 oxidizes to $C_6H_5CO_2H$; (b) KOH fusion yields α toluic acid and formic acid.

Phenyl-propionic acid, $C_6H_5.C \equiv C.CO_2H$, m.p. $136^\circ-137^\circ$.

o-Coumaric acid, m.p. 208° (with decomp.). Yields $C_6H_4 \begin{smallmatrix} < OH \\ CO_2H \end{smallmatrix} \begin{smallmatrix} (1) \\ (2) \end{smallmatrix}$ and CH_3CO_2H . Alk. salt solns. yellow with green fluorescence.

C. HYDROXY ACIDS.¹

(a) To a neutral solution add 2 or 3 drops of 10% FeCl_3 soln.

(a) Hydroxy acids produce a yellow coloration ;
 α -hydroxy acids a strong yellow colour.
 Hence test for following :—

Glycollic acid, $\text{CH}_2.\text{OH}.\text{CO}.\text{OH}$, m.p. 80° .

Lactic acid, $\text{CH}_3.\text{CH}.\text{OH}.\text{CO}.\text{OH}$, S.G.

1'215.

(i.) CrO_3 oxidizes it to acetic acid and CO_2 .

(ii.) Heat 1 c.c. with 2 c.c. conc. H_2SO_4 to 130° ;
 aldehyde and formic acid are evolved.

Hydracrylic acid, $\text{CH}_2.(\text{OH}).\text{CH}_2.\text{CO}.\text{OH}$.

A thick syrup. Boiled with H_2SO_4 ,
 diluted with an equal bulk of water, it
 yields acrylic acid (which see).

Glyceric acid, $\text{CH}_2.\text{OH}.\text{CH}.\text{OH}.\text{CO}.\text{OH}$.

A syrup. Fused with KOH yields
 $\text{CH}_3.\text{CO}.\text{OH}$ and $\text{H}.\text{CO}.\text{OH}$.

Tartronic acid, $\text{CH}.\text{OH}:(\text{CO}.\text{OH})_2$, m.p.

184° . Ca and Ba salts pptd. from neutral
 solns.

Malic acid, $\begin{array}{c} \text{CH}_2.\text{CO}.\text{OH} \\ | \\ \text{CH}.\text{OH}.\text{CO}.\text{OH} \end{array}$ m.p. 100° .

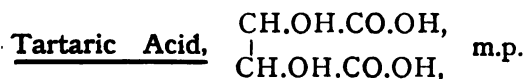
(CaCl_2 ppts. Ca salt on boiling from
 neutral solutions.)

¹ Colour reactions are produced with β -naphthol sulphuric acid [E. Pinuera, *Chem. News*, vol. 75, 1941]. The reagent is made by dissolving 0.02 gram β -naphthol in 1 c.c. H_2SO_4 (s.g. 1.83). To 0.05 gram of substance in a basin add 10 to 15 drops of the reagent (1), then gradually heat (2) ; cool and add 15 to 20 c.c. water (3) :—

(a) Tartaric acid produces (1) blue colour, (2) green colour, (3) persistent reddish-yellow soln.

(b) Citric acid produces (1) intense blue, (2) no change, (3) light yellow soln.

(c) Malic acid produces (1) greenish-yellow, (2) bright yellow, (3) bright orange soln.



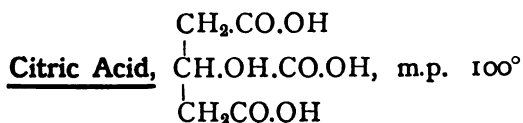
167–170°. Colourless, transparent, crystalline solid ; easily soluble in water and alcohol. $[\alpha]_D \pm$.

1. Acids and tartrates heated in dry state swell up, blacken, and give odour of burnt sugar.
2. Acids and tartrates heated with conc. H_2SO_4 blacken and evolve SO_2 , CO_2 , and CO .
3. CaCl_2 to a neutral soln. of a tartrate gives white ppt. of calcium tartrate, soluble in acetic acid ; very weak solns. require shaking and standing for a time. The ppt. is soluble in cold NaOH or KOH soln. ; repptd. on heating, and redissolving on cooling.
4. AgNO_3 to a neutral soln. of tartrate gives white ppt. of silver tartrate ; allow ppt. to settle, pour off supernatant liquid, and dissolve ppt. in just sufficient dilute NH_4OH ; gently warm, when metallic Ag is pptd. If test-tube perfectly clean a mirror will be obtained.
5. Tartaric acid and tartrates of alkalis prevent precipitation of copper hydrate from a soln. of copper sulphate by NaOH or KOH soln.

Saccharic acid, $\text{C}_6\text{H}_4(\text{OH})_4(\text{CO.OH})_2$. Deliquescent gummy mass ; $\text{C}_6\text{H}_5\text{NHNH}_2$, yields a diphenylhydrazide, m.p. 210°.

Mucic acid, $\text{C}_6\text{H}_4(\text{OH})_4(\text{CO.OH})_2$. White crys. powder, m.p. 210°. (decompn.).

- (i) $\text{CH}_3\text{CO.Cl}$ yields tetra-acetate, m.p. 177°.
- (ii) Heated with $\text{C}_2\text{H}_5\text{OH}$ and H_2SO_4 yields diethyl ester, m.p. 158°.



(crys.). White crys; solid ; very soluble in water and alcohol, and insoluble in ether.

1. Dry acid when heated melts and slowly darkens ; pungent fumes of aconitic acid, $\text{C}_6\text{H}_6\text{O}_6$, evolved, which are very irritating.
2. Acid or citrates heated with conc. H_2SO_4 evolve CO and CO_2 , and after prolonged heating evolve SO_2 without blackening.
3. CaCl_2 soln., added to a neutral soln. of a citrate, gives no ppt. in cold, but on boiling a white crys. ppt. of calcium citrate is produced, insoluble in KOH soln. ; the ppt. is formed more readily if soln. is slightly alkaline.
4. AgNO_3 reacts similarly to tartrates, but reduction is not so readily produced.

Mandelic acid, $\text{C}_6\text{H}_5\text{CH.OH.CO.OH}$, m.p. 132.8° . Slightly soluble in cold water ; oxidized to $\text{C}_6\text{H}_5\text{COOH}$ by boiling with dil. HNO_3 :

(β) o-Hydroxy acids produce a violet coloration. (Volatile in water vapour and soluble in CHCl_3 .)

Salicylic Acid, $\text{C}_6\text{H}_4\text{CO}_2\text{H.OH}(1.2)$, m.p. 155° . Crystalline solid, soluble in water and alcohol, very soluble in chloroform.

1. FeCl_3 to neutral soln. gives violet coln. ; discharged by HCl, but not by acetic acid.

2. 0.5 gram acid or salicylate, heated with 1 c.c. CH_3OH and 2 c.c. conc. H_2SO_4 , gives fragrant odour of oil of wintergreen (methyl salicylate).
3. Heated with soda-lime, phenol is given off.

(γ) o-Dihydroxy m. acid (*e.g.* protocatechuic acid, $\text{C}_6\text{H}_3(\text{OH})_2\text{COOH}$ (1.2.4) or any of its derivatives) produce a blue colour after addition of a few drops of dilute NaOH .

Protocatechuic acid, $\text{C}_6\text{H}_3(\text{OH})_2\text{CO}_2\text{H}$ (1.2.4), m.p. 190°C . of the anhydrous acid, soluble in water.

1. FeCl_3 to soln. of the acid gives a green coloration, turning blue after addition of very dilute NaOH soln., and finally red.
2. FeSO_4 soln. gives a violet coloration with acid soln.
3. Ammoniacal AgNO_3 reduced to metallic Ag .

(δ) Trihydroxy monobasic acids—a bluish-black or dark blue ppt. given by certain of these, *e.g.*—

Gallic acid, $\text{C}_6\text{H}_2\text{CO}_2\text{H}(\text{OH})_3$ (1.3.4.5), m.p. 220° with decomposition; difficultly soluble in cold water, readily in hot; soluble in alcohol and ether.

1. FeCl_3 soln. gives blackish-blue coloration to soln. of acid.
2. $\text{Ca}(\text{OH})_2$ soln., when in slight excess, gives a blue colour to a soln. of the acid; in great excess a blue ppt., turning finally black.
3. Gelatine soln. gives no ppt. with soln. of gallic acid.

Tannic acid, $\text{C}_{14}\text{H}_{10}\text{O}_9 \cdot 2\text{H}_2\text{O}$. Colourless amorphous solid, easily soluble in water;

soluble in dilute alcohol, and almost insoluble in dry ether.

1. FeCl_3 soln. to soln. of acid or tannates a blue-black ppt.
2. $\text{Ca}(\text{OH})_2$ soln. gives a white ppt. (or grey) of calcium tannate.
3. Tannic acid soln. gives a white or greyish-white ppt. when added to a freshly prepared soln. of gelatine.

(b) If no colour produced with FeCl_3 , test especially for—

- (a) m-Hydroxy acids, which give a reddish-brown when heated with conc. H_2SO_4 .
- (β) p-Hydroxy acids boiled with conc. HCl yield a phenol and CO_2 .

All hydroxy acids—

- (i) When acted upon by acid chloride, yield esters in which acid residue enters the alcohol-OH group.
- (ii) When acted upon by a mixture of conc. HNO_3 and H_2SO_4 have the H of the alcoholic OH group replaced by NO_2 group.

These two reactions can be applied to prepare the alcohol esters and nitrates, and hence used as a means of identifying acid.

(C) Test specially for aldehyde or ketonic acids.

- (1) Glyoxylic acid, $\text{CHO}.\text{CO}_2\text{H}$, a thick liquid, sol. in water.
 - (i.) Reduces ammoniacal AgNO_3 , giving a mirror.
 - (ii.) Forms a hydrazone with $\text{C}_6\text{H}_5\text{NH}.\text{NH}_2$.
 - (iii.) AgNO_3 gives white crys. ppt.
- (2) Pyroracemic acid (α ketopropionic acid), $\text{CH}_3.\text{CO}.\text{CO}_2\text{H}$, b.p. $165-170^\circ$ (decomposes).
 - (i.) Reduces ammoniacal, AgNO_3 .
 - (ii.) Sols. of its salts give red coloration with FeCl_3 .
 - (iii.) Readily forms a hydrazone with $\text{C}_6\text{H}_5\text{NH}.\text{NH}_2$, m.p. 182° .

- (3) Aceto-acetic acid, $\text{CH}_3\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$. Thick liquid miscible with water.
- (i.) Heated yields CO_2 and $(\text{CH}_3)_2\text{CO}$.
 - (ii.) FeCl_3 gives violet-red coloration as also does its esters.
- (4) Lævulic acid, $\text{CH}_3\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, m.p. 33° .
- (i.) AgNO_3 gives white ppt. from neutral sols.
 - (ii.) Forms hydrazone, m.p. 108° .

(2) If the acid cannot be identified by any of the above reactions, the following experiments should be carried out:—

- (a) Mix 2 to 3 grams of the acid with 10 c.c. of absolute alcohol, and conduct into the mixture dry HCl gas till no more absorption takes place. Heat this mixture under reflux for 30 minutes, cool, and separate ester by diluting with large bulk of water, when it will settle out; if a portion does not separate the ester by this treatment or by salting out, then it must be separated by distillation (see viii. 2 (2)). Determine b.p.
- (b) The eqt. wt. of the acid should be determined as in VIII. 1.
- (c) Prepare the Ag or Pb salt, and determine eqt. wt. Dissolve 1 to 2 grams of the acid in as small amount of water as possible, and neutralize the soln. so formed with a soln. of Na_2CO_3 , boiling to expel the CO_2 produced. Cool the soln., and add a soln. of AgNO_3 till no further precipitate is produced; filter at the pump and wash with cold water, keeping the silver salt covered up as much as possible from the light; dry the silver salt in a basin over the water-bath. When completely dry, weigh out into a tared crucible from 0.5 to 1 gram of the Ag salt; carefully heat the salt in the crucible, and as decomposition proceeds raise the temperature to a low red heat: cool

and weigh the residual Ag: repeat and weigh till constant.

If acid is insoluble in water, dissolve 1 to 2 grams of it in 10% NaOH soln., using no more than is necessary to combine with the acid to form the sodium salt, bringing solution to neutral point with dil. HNO_3 in the event of too much NaOH being used: proceed as above.

N.B.—If warm AgNO_3 soln. be added to the hot soln. of the sodium salt, and the resulting soln. allowed to cool, many of the Ag salts can be obtained in a crystalline form, and hence washed and dried more quickly than when in the powder form:

TABLE FOR IDENTIFICATION OF ANY ONE OF THE COMMONER ACIDS
OR THEIR SALTS.

- I. Prepare a neutral solution from the acid by dissolving it in Na_2CO_3 soln., or if a salt, boil with Na_2CO_3 soln.; filter off from precipitated insoluble carbonates, if any, and just acidify the filtrate by adding HNO_3 to the boiling soln.; then add NH_4OH drop by drop till just alkaline, and boil off excess of NH_3 . Great care should be taken in obtaining a perfectly neutral soln.
- II. Test portions of this solution as follows:—
 - A. Add neutral FeCl_3 soln.
 - (a) Red coloration produced.
 - (i.) Instantly discharged by HCl to yellow colour. **Formic and acetic acids.**
 - (ii.) Not discharged by HCl.
 - (a) Discharged by HgCl_2 soln., or by nascent H (Zn and H_2SO_4). **(Sulphocyanic acid.)**
 - (b) Not discharged by HgCl_2 soln. or by nascent H (Zn and H_2SO_4). **Meconic acid.**
 - (iii.) Blackened by excess of KOH soln. **(Pyrogallic acid.)**
 - (b) Purple coloration produced.
 - (i.) Instantly discharged by HCl to yellow colour.
 - (a) Not discharged by acetic acid. **Salicylic acid.**
 - (b) Discharged by acetic acid. **(Phenol.)**
 - (c) Coloured precipitate produced.
 - (i.) Buff-coloured, dissolved by HCl with separation of white crystalline solid. **Benzoic acid, (Hippuric and) Cinnamic acids.**

- (ii.) Reddish-brown, dissolved by HCl to clear soln. **Succinic and Phthalic acids.**
(Uric acid; gives white crys. with HCl.)
- (iii.) Blue-black, dissolved by H_2SO_4 to yellowish or brown soln. **Gallic and tannic acids.**
- (iv.) Prussian blue, dissolved by NaOH soln., with formation of insol. reddish-brown $Fe_2(OH)_6$. **Ferrocyanic acid.**
- (v.) Brown coloration, giving Prussian blue on adding SO_2 soln. **Ferriecyanic acid.**
- B. Add neutral $CaCl_2$ soln. to the cold soln.
- (a) White precipitate produced.
- (i.a) Sol. on boiling. **Malonic.**
- (i.) Fine pulverulent powder, insol. in acetic acid, sol. in HCl. **Oxalic acid.**
- (ii.) Heavy cryst. powder, sol. in acetic acid and sol. in HCl. **Tartaric, Tartronic and Fumaric acid.**
- (b) White ppt. after boiling and adding one drop of NH_4OH , sol. in acetic acid. **Citric acid.**
- (c) White ppt. after boiling and adding an equal volume of alcohol, sol. in acetic acid. **Malic acid.**
- (d) Greyish-white ppt., sol. in HCl to a pinkish soln. **Tannic and gallic acids.**

2. PHENOLS. The phenol may be identified by forming benzoyl ester with C_6H_5COCl (or one of its derivatives), separating and det. m.p. or b.p. (Schotten-Baumann Reaction).¹

- (1) (i.) Monohydric Phenols. Those of low molecular weight are slightly soluble, but solubility decreases with increase of molecular weight. Sol. in NaOH soln.
- (ii.) Dihydric Phenols. More soluble; soluble in Na_2CO_3 soln.
- (iii.) Trihydric Phenols. More soluble still in water and in Na_2CO_3 soln.

¹ Take from 0.5 to 1 gram of substance in a test-tube with 5 c.c. H_2O ; then add 1 c.c. C_6H_5COCl and soln. of NaOH (1 in 10) till soln. alkaline; well shake till smell of C_6H_5COCl has disappeared. Then pour into large excess of water, when the benzoyl derivative will settle out. If it does not solidify at once, allow it to stand some minutes, when it will gradually crystallize. Separate it, well wash with water, dry, and determine m.p.

- (2) Carefully add 2 c.c. of CH_3COCl to 1 gram of a phenol, warm if necessary, and then carefully pour into 10 c.c. of water ; an oil will settle out due to the formation of an ester of acetic acid. It can be separated, dried, and b.p. detd.
- (2a) Use $\text{C}_6\text{H}_5\text{COCl}$ instead of CH_3COCl , followed by NaOH in excess, etc. (see IX. 2).
- (3) FeCl_3 soln. added to a solution of a phenol produces a coloration discharged by HCl .
- (i.) Monohydric—mostly violet to blue. (Thymol produces no colour.)
 - (ii.) Dihydric (ortho)—green coloration.
 - (iii.) „ (meta)—violet.
 - (iv.) Trihydric—green, violet, blue to black.

Colour reactions of Polyphenols and their Isomers

(E. P. Alvarez, *Chem. News*, vol. 91, p. 125).

In a porcelain basin of 30 c.c. capacity are placed 0.2 gram of yellow, granulated, perfectly dry sodium dioxide ; immediately afterwards 0.04 or 0.05 gram of the polyphenol to be tested, and then 5 c.c. of absolute alcohol. These substances are allowed to remain in contact with one another from 4 to 6 minutes ; whilst the reaction is taking place, the liquid is kept in motion by imparting a slight circular movement to the basin ; finally, 15 c.c. cold distilled water is added. Colours are produced on adding the alcohol, which may change after a few minutes, and which may or may not change on adding the water, viz.—

$\text{C}_6\text{H}_4 \begin{smallmatrix} \text{OH} \\ \diagup \\ \text{OH} \end{smallmatrix}$ (1) gives pale pink, then green to
(2) bronze, and finally red-brown liquid.

$\text{C}_6\text{H}_4 \begin{smallmatrix} \text{OH} \\ \diagup \\ \text{OH} \end{smallmatrix}$ (1) gives intense reddish-yellow,
(3) transitory blue, orange-coloured liquid.

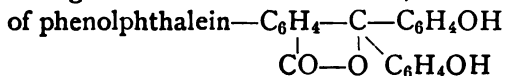
$\text{C}_6\text{H}_4 \begin{smallmatrix} \text{OH} \\ \diagup \\ \text{OH} \end{smallmatrix}$ (1) gives reddish-brown or dull red,
(4) remains same, intense red liquid.

All the phenols examined gave similar series of changes, viz. pyrogallol, oxyhydroquinone (1.2.4), phloroglucine, orcine, homopyrocatechin, thymohydroquinone.

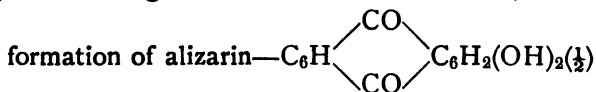
EXCEPTIONS (with FeCl_3 soln.).—

- (a) Paradihydric phenols are oxidized to quinones, which settle out in golden-yellow crystals.
 - (b) α -Naphthol gives a white to violet ppt. of dinaphthol; β -naphthol, green to white.
 - (c) Nitrophenols, meta, and para oxyacids do not produce any colour.
4. Heat in a small test-tube for 1 to 2 mins. to about 150°C . (do not char) 0.2 gram of a phenol with 0.2 gram of phthalic anhydride moistened with a drop or two of conc. H_2SO_4 or 0.2 gram of ZnCl_2 . Cool and treat fused mass with 20 c.c. of cold water, and then add NaOH soln. very gradually, till no further change occurs. Coloured solutions will be obtained, some of which will fluoresce, especially the m. dihydric phenols.

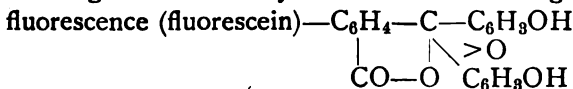
Phenol gives an intense red solution, due to formation of phenolphthalein—



Pyrocatechin gives an intense blue solution, due to



Resorcin gives an intense yellowish red soln. with green fluorescence (fluorescein)—



Pyrogallol gives an intense blue, due to formation of gallein.

- (5) Add saturated Br water to 5 c.c. of a phenol soln. till soln. is yellow: white ppt. of a tribromphenol will settle out.

- (6) **Liebermann's Reaction:** To 0.05 gram of a saturated phenol add 5 or 6 drops of conc. H_2SO_4 , and then 0.01 gram of KNO_2 : a deep blue or green coloration is obtained. Pour into water: it turns red, and on adding excess of alkali, blue or green. (All phenols do not give this reaction.)

The following are the more common phenols :—

- (1) **Phenol**, $\text{C}_6\text{H}_5\text{OH}$, m.p. 43° . Colourless crys. mass gradually acquiring a reddish colour on exposure to the air; sol. in water, very easily sol. in alcohol and ether.

(1) FeCl_3 soln. to soln. of phenol produces violet coloration, discharged by HCl , acetic acid, or alkalies.

(2) Br water to aqueous soln. gives white ppt. of tribromophenol, $\text{C}_6\text{H}_2\text{Br}_3\text{OH}$.

(3) Bleaching powder soln. added to an aqueous soln. of phenol produces a violet coloration; if NH_4OH be added first, the colour is blue.

(4) Gives Liebermann's reaction.

(5) Produces phenolphthalein with phthalic anhydride.

- (2) **Carvacrol**, C_6H_3 $\begin{array}{l} \text{CH}_3 \text{ (1)} \\ \text{—CH(CH}_3\text{)}_2 \text{ (2), b.p. } 236^\circ \text{ C.; S.G. } 0.981. \\ \text{OH (4)} \end{array}$

FeCl_3 produces green coloration with alcoholic soln.

- (3) **Thymol**, C_6H_3 $\begin{array}{l} \text{CH}_3 \text{ (1)} \\ \text{—OH (3), m.p. } 51.5^\circ. \text{ 10 c.c. of} \\ \text{CH(CH}_3\text{)}_2 \text{ (4)} \end{array}$

aqueous soln. treated with 1 c.c. acetic acid and 2 c.c. H_2SO_4 gives on warming red-violet coloration.

- (4) **Pyrocatechin**, $\text{C}_6\text{H}_4(\text{OH})_2$ (1,2), m.p. 104° . White crys. solid, easily sol. in water.

(1) To 5 c.c. of aqueous soln. add excess of KOH soln. and well shake with air: the soln. turns green, then brown, and finally black.

(2) To 5 c.c. of aq. soln. add $\text{Pb}(\text{CH}_3\text{CO}_2)_2$ soln. A white ppt. of $\text{PbC}_6\text{H}_4\text{O}_2$ is produced.

(3) FeCl_3 soln. added to aq. soln. gives an emerald green colour, changed to violet-red on adding a soln. of NaHCO_3 .

(4) Ammoniacal AgNO_3 soln. is reduced to metallic Ag by cold soln. of pyrocatechin.

(5) Alkaline copper sulphate soln. is reduced to Cu_2O by hot soln. of pyrocatechin.

- (6) Produces alizarin with phthalic anhydride.
- (5) Resorcin, $C_6H_4(OH)_2$ (1.3), m.p. 118° . White crys. solid, easily sol. in water, alcohol, and ether; insol. in $CHCl_3$ and CS_2 .
- (1) Heat 0.1 gram resorcin with 1 c.c. conc. H_2SO_4 and 0.1 gram powdered $NaNO_2$; pour melt into 10 c.c. water, and make soln. alkaline with NH_4OH ; add 2 c.c. fusel oil and well shake: on standing, the fusel oil separates and is coloured carmine-red, showing a cinnabar-red fluorescence.
 - (2) Add 0.01 gram resorcin to 1 c.c. conc. H_2SO_4 in a crucible; then add about 0.1 gram of tartaric acid; heat to about $120^\circ C.$: a beautiful reddish-violet coloration produced.
 - (3) Produces fluorescein with phthalic anhydride.
 - (4) Produces a tribom-derivative with Br.
- (6) Hydroquinone, $C_6H_4(OH)_2$ (1.4), m.p. 169° . Readily sol. in water, alcohol, and ether; difficultly sol. in cold benzene.
- (1) NH_4OH added to an aq. soln. produces a reddish-brown soln.
 - (2) $FeCl_3$ added to an aq. soln. gives yellow crys. ppt. of quinone with penetrating characteristic odour.
 - (3) Aqueous soln. gently heated with MnO_2 and H_2SO_4 produces quinone, and odour is more strongly developed.
- (7) Cresorcinol, $C_6H_3<\begin{smallmatrix} CH_3 \\ (OH)_2 \end{smallmatrix}$ (1), m.p. $104-105^\circ$. $FeCl_3$ to aq. soln. gives greenish-blue coloration.
- (8) Orcinol, $C_6H_3<\begin{smallmatrix} CH_3 \\ (OH)_2 \end{smallmatrix}$ (3.5), m.p. 107° (anhydrous). Easily sol. in water, alcohol, and ether.
- (1) $FeCl_3$ to aq. soln. gives deep blue-violet.
 - (2) To aq. soln. add KOH soln. and few drops of $CHCl_3$, and then warm: a purple soln. turning fiery red is produced, which on diluting with water gives an intense fluorescence.
- (9) Pyrogallol, $C_6H_3(OH)_3$ (1.2.3), m.p. 131° . White crys. solid, easily sol. in water, with difficulty in alcohol and ether.
- (1) $FeCl_3$ soln. to soln. of pyrogallol gives fine blue colour, which gradually fades.
 - (2) KOH soln. in excess to pyrogallol soln. gives on shaking with air, a yellow turning to deep brown coloration.

(3) AgNO_3 soln. gives an immediate dark brown ppt. of metallic Ag.

(4) Produces gallein with phthalic anhydride.

(10) Phloroglucinol, $\text{C}_6\text{H}_3(\text{OH})_3$ (1.3.5), m.p. 217° . (i.) To aq. soln. add KNO_2 soln. and $\text{C}_6\text{H}_5\text{NH}_2\cdot\text{HNO}_3$ soln.: a cinnabar-red ppt. of benzeneazophloroglucinol obtained. (ii.) Dip a pine shaving (matchwood) in HCl , and then into aq. soln.: a deep red coloration.

(11) α -Naphthol, $\text{C}_{10}\text{H}_7\text{OH}$, m.p. 95° . Difficultly sol. in hot water, easily sol. in $\text{C}_2\text{H}_5\text{OH}$, $(\text{C}_2\text{H}_5)_2\text{O}$, CHCl_3 , or C_6H_6 . Soln. of bleaching powder to aq. soln. gives a deep violet coloration, and then dark violet ppt.

(12) β -Naphthol, $\text{C}_{10}\text{H}_7\text{OH}$, m.p. 122° . Easily sol. in hot water. Bleaching powder a yellow coloration, disappearing on adding excess.

Both naphthols give red-coloured azo dyes when coupled to diazotized $\text{C}_6\text{H}_5\text{NH}_2\text{HCl}$.

Both, when heated in strong aqueous alkali soln. with CHCl_3 to 50° , give a Berlin blue colour, gradually changing through green to brown.

3. ALDEHYDES AND KETONES.

Aldehydes and ketones are best liberated from their bisulphite derivatives by heating with a soln. of Na_2CO_3 or K_2CO_3 .

(1) TOLLEN'S REACTION. In a test-tube cleaned with hot NaOH solution and then distilled water, place 2 c.c. AgNO_3 soln., and then NH_4OH soln. drop by drop till ppt. first formed is just redissolved. Then add 1 c.c. NaOH soln.; shake the mixture round the tube, and then allow 2 or 3 drops of an aldehyde solution to flow down the moistened surface. An immediate deposit of Ag is obtained (do not warm).

(1a) Repeat above expt. without NaOH , and warm if necessary.

NOTE.—This reaction is also given by other compounds, *e.g.* di- and trihydric phenols, amido phenols, certain hydroxy-acids, *e.g.* tartaric and citric, etc. (These reactions not given by ketones.)

- (2) CARO'S REACTION. Add 2 or 3 drops of an aldehyde soln. to 5 c.c. of Schiff's reagent (fuchsine solution which has been just decolorized by SO_2); the colour is restored.

NOTE.—Some ketones will react similarly if in large quantity and allowed to act for some time.

- (3) Add about 0.1 gram of diazo-benzene-sulphonic acid to 5 c.c. of water, then a few drops of NaOH and a few drops of an aldehyde soln., and finally a small piece of Na amalgam (size of a pea); a red-violet colour is produced.

Diazo-benzene-sulphonic acid, $\text{C}_6\text{H}_4\text{SO}_2\text{N}_2\text{O}$, is prepared as follows:—

Dissolve 2 grams sulphanilic acid in smallest amount of Na_2CO_3 soln.; add 1 gram of KNO_3 dissolved in 5 c.c. of water. Pour this solution slowly into 10 c.c. of dilute H_2SO_4 (1 acid to 9 water), keeping the solutions well cooled. The diazo compound separates as a crys. solid on standing.

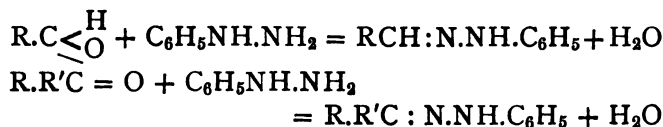
- (4) Make 10 c.c. of a cold saturated soln. of sodium bisulphite. To this add 2 to 3 c.c. of a saturated aldehyde soln. (or 1 c.c. of free aldehyde) and well shake. A crystalline solid settles out of aldehyde sulphite. Separate these crystals, wash with a little cold water. Then mix with some Na_2CO_3 soln., and distil into a test-tube containing 1 c.c. of water; prove that aldehyde is in distillate by (2).

NOTE.—Ketones produce similar crystalline compounds.

- (5) To 5 c.c. water add 2 c.c. $\text{C}_6\text{H}_5\text{NH.NH}_2$, and then 3 c.c. of glacial acetic acid in 5 c.c. H_2O : now add 1 c.c. of the aldehyde (or 5 to 10 c.c. of a saturated soln.). Heat the mixture¹ on a water-bath, when a hydrazone of the aldehyde will settle out after some time. If

¹ This reaction is best carried out in a loosely stoppered test-tube.

solid it can be crystallized from water, alcohol, or benzene, and its m.p. determined (see XI. 9 for m.p. of few common ones). The hydrazones of lower fatty aldehydes are oily liquids, and difficult to purify.



- (6) Dissolve 0.5 gram of free semicarbazide ($\text{NH}_2\text{CO.NH.NH}_2$) in as little water as possible, add 0.5 c.c. acetic acid, and then 1 c.c. of aldehyde or ketone and sufficient methyl or ethyl alcohol to give a clear soln., which is heated on a water-bath for 15 minutes. A *semicarbazone* settles out, which may be recrystallized from alcohol and its m.p. determined.¹



- (7) Warm 2 c.c. KOH soln. with 1 c.c. of aldehyde soln. : yellow colour is produced and a resinous mass separates. (This reaction given by fatty aldehydes.)
 (8) Aromatic aldehydes, when treated with alkalis as in (6), yield alcohols and acids, *e.g.*—



To 1 c.c. of the aldehyde add 5 c.c. of 10 % alcoholic soln. of potash ; well shake ; allow to stand : a solid settles out. Filter and wash ppt. with a little alcohol. Dissolve ppt. (K salt) in water, and acidify with HCl, when the free acid is pptd., and can be identified. The alcoholic soln. contains an aromatic alcohol, which is left on carefully evaporating the alcohol off.

- (9) Aromatic aldehydes also yield condensation products with anilines ; viz. formation of malachite green from

¹ *J.C.S.*, 1905, A i. 179.

benzaldehyde. Heat 1 c.c. benzaldehyde and 1 c.c. dimethylaniline and 1 gram fused ZnCl_2 in crucible to $100-110^\circ \text{C}$.; cool and transfer to basin, and boil with water and a little HCl ; to this add a little PbO_2 in cold, when green colour is obtained.

The following are amongst the more common :—

Formaldehyde, $\text{H}\cdot\text{CHO}$. Only known in solution or as a gas. Commercially appears as formalin, which is a solution of 35 to 40 per cent. of formalin, containing also methyl alcohol.

1. Gallic acid test : Mix 0.2 c.c. of a saturated soln. of gallic acid in pure ethyl alcohol with 1 to 2 c.c. of a weak soln. of formaldehyde, and then carefully add down side of tube 3 to 5 c.c. conc. H_2SO_4 to form a layer: a green zone appears at the line of contact of the two liquids, which gradually changes to a pure blue ring.
2. Methylene di- β naphthol test :¹ Place in a test-tube 10 drops of a 10 % soln. of formaldehyde, 3 c.c. dil. alcohol (1 to 2), 0.04 to 0.06 gram β naphthol, and 3 to 5 drops of conc. HCl . Boil gently till liquid becomes filled with an abundant ppt. of small white needles. Filter while hot. Wash ppt. with 1 c.c. dil. alcohol (1 to 2). Boil ppt. with 4 c.c. dil. alcohol (1 to 1). Cool and filter off ppt. ; wash with 1 c.c. dil. alcohol. Dry on porous plate in warm, and determine m.p. of the methylene di- β naphthol so obtained. m.p. = $189-192^\circ$, with decomposition to a brown liquid.

Paraformaldehyde, $(\text{H}\cdot\text{CHO})_n$. Amorphous solid, sol. in warm water, giving the odour of formaldehyde. The solution gives the reaction of formaldehyde.

Metaformaldehyde, $(\text{H}\cdot\text{CHO})_3$, m.p. 171° . White solid, insol. in water, alcohol, and ether ; by boiling, gives an aqueous soln. which shows the reaction for formaldehyde.

Acetaldehyde, $\text{CH}_3\cdot\text{CHO}$, b.p. 20.8° . Mostly used as an aqueous soln.

1. Gives all the characteristic reaction of aldehydes.

¹ Mulliken, " Identification of Pure Organic Compounds."

2. To 5 c.c. aqueous soln., add a drop of an aqueous soln. of phenol, and then carefully add 2 c.c. conc. H_2SO_4 : an orange-yellow colour is produced where two liquids meet, and a ppt. if solution is strong. H.CHO gives a bright crimson colour under same conditions (Hehner). Aldehyde semi-carbazone m.p. 162° .

Paraldehyde, $(\text{CH}_3\text{CHO})_3$. Colourless liquid, b.p. 124° ; changed to ordinary aldehyde on distilling with H_2SO_4 .

Metaldehyde, $(\text{CH}_3\text{CHO})_n$. White crys. solid, insol. in water; sublimes at $112-115^\circ$, and produces ordinary aldehyde.

Acrolein, $\text{CH}_2 = \text{CH.CHO}$, b.p. 52° . S.G. 0.841 @ 20° .

Crotonaldehyde, $\text{CH}_3\text{CH} = \text{CH.CHO}$, b.p. 104° . S.G. 1.033 @ 0° .

Benzaldehyde, $\text{C}_6\text{H}_5\text{CHO}$, b.p. 179° . S.G. 1.0504 . Colourless liquid, with odour of "bitter-almond oil"; slightly sol. in water; miscible with alcohol and ether.

1. Easily oxidized to benzoic acid. Shake up 0.5 c.c. of liquid with 10 c.c. alk. KMnO_4 , filter off ppt. of hydrated MnO_2 , and test filtrate for $\text{C}_6\text{H}_5\text{COOK}$.

Cumicaldehyde, $\text{C}_6\text{H}_4.\text{C}_3\text{H}_7.\text{CHO}$ (1.3), b.p. 235° . S.G. 0.9832 @ 0° .

Cinnamicaldehyde, $\text{C}_6\text{H}_5.\text{CH}:\text{CH.CHO}$, b.p. 247° . S.G. 1.0497 @ 20° .

Acetone, $(\text{CH}_3)_2\text{CO}$, b.p. 56.5° . S.G. 0.7994 @ 13.9° . Colourless, mobile liquid, with peculiar odour; miscible with H_2O , $\text{C}_2\text{H}_5\text{OH}$, and $(\text{C}_2\text{H}_5)_2\text{O}$.

1. To an aqueous soln. add 5 c.c. of 10% Na_2CO_3 , and then soln. of I in KI till soln. coloured strongly yellow; gently warm, when iodoform will be formed, which is recognized by its odour and settling out as a yellow crys. solid. Acetone-semi-carbazone m.p. 187° .

Methyl Nonylketone, $\text{CH}_3\text{CO.C}_8\text{H}_{17}$, m.p. 15° , b.p. 225° (chief const. of oil of rue).

Acetophenone, $\text{C}_6\text{H}_5\text{CO.CH}_3$, m.p. 26.5° , b.p. 202° . Semi-carbazone, m.p. 198° .

Benzophenone, $\text{C}_6\text{H}_5\text{CO.C}_6\text{H}_5$, m.p. $48-49^\circ$. Semi-carbazone m.p. 164° .

Benzoin, $\text{C}_6\text{H}_5\text{CH(OH).CO.C}_6\text{H}_5$, m.p. 134° .

Benzil, $C_6H_5CO.CO.C_6H_5$, m.p. 90° . Mono-semi-carbazone, m.p. 174° .

Furfural, $C_4H_3O.CH_2O$, b.p. 162° (see Pentoses).¹

Menthone, $C_{10}H_{18}O$, b.p. 206° . S.G. 0.897.

Ionone, $C_{13}H_{20}O$, b.p. $126^\circ-128^\circ$ @ 12 m.m. S.G. 0.9351 (artificial violet perfume).

Methyl-amyl Ketone, $CH_3.CO.C_5H_{11}$, b.p. 151° . S.G. 0.837 @ 50° .

Camphor, $C_{15}H_{26}O$, , m.p. 175° C., b.p. 204° (sublimes), sparingly sol. in water, alkalies, or acids; sol. in $(C_2H_5)_2O$, $CHCl_3$, $(CH_3)_2CO$, CH_3CO_2H , CS_2 , and fixed oils.

Chief derivatives for identification are:— $C_{10}H_{15}OBr$, m.p. 76° (by Br. in $CHCl_3$), $C_{10}H_{16}NOH$, m.p. 118° (by NH_2OH in alk. soln.), does not form bi-sulphite nor re-act with $CH_3CO.Cl$.

4. QUINONES. Yellow (orange to red) crys. solids, peculiar odour, volatile either alone or in steam. SO_2 solution reduces them to colourless dihydroxy compounds.

Quinone, $C_6H_4O_2$, m.p. 116° . Golden-yellow crys. solid; easily sol. in hot water, alcohol, and ether.

1. To aqueous soln. add a little SO_2 soln.: the soln. turns brown owing to the formation of quinhydrone, $C_6H_4O_2.C_6H_4(OH)_2$; on adding excess of SO_2 the soln. becomes colourless, owing to the formation of hydroquinone.

Anthraquinone, $C_6H_4(CO)_2.C_6H_4$, m.p. 285° . Yellow crys. solid; easily sol. in hot benzene.

1. SO_2 does not reduce it.
2. Zn dust and $NaOH$ soln. produce oxanthranol (see VI. 4 (iii)).

Naphthaquinone, $C_{10}H_6O_2(1.4)$. Yellow crys. solid, m.p. 125° ; characteristic odour; volatile in steam.

¹ *Reaction of furfural derivatives* (H. J. Fenton, B.A. Report, 1904).—When methyl furfural is heated with $C_6H_5N(CH_3)_2$ and $POCl_3$ or $ZnCl_2$ or dry $H_2C_2O_4$, an intensely blue-coloured compound is produced; given also by brommethylfurfural and its chloro-, iodo-, and acetoxy derivatives.

β Naphthaquinone, $C_{10}H_6O_2$ (1.2). Orange crys. solid ; odourless and non-volatile ; decomposes at 115–120°.

Phenanthraquinone. Orange-yellow crys. solid ; sparingly sol. in water or cold alcohol ; easily sol. in hot alcohol, ether, and benzene ; sol. in conc. H_2SO_4 to a dark green soln.

5. PHENOL ALCOHOLS AND PHENOL ALDEHYDES AND ETHERS. These possess properties of phenols, alcohols, and aldehydes.

The esters of these compounds are important. The commonest are—

Saligenin, $C_6H_4 \begin{smallmatrix} \text{OH} \\ \text{CH}_2\text{OH} \end{smallmatrix} \begin{smallmatrix} (1) \\ (2) \end{smallmatrix}$, m.p. 82°. $FeCl_3$ gives deep blue colour to its solutions.

Guaiacol, $C_6H_4 \begin{smallmatrix} \text{OCH}_3 \\ \text{OH} \end{smallmatrix}$, b.p. 200°. Colourless liquid, sparingly sol. in water, easily in alcohol and ether.

(1) $FeCl_3$ soln. to alcoholic soln. produces emerald-green coloration.

(2) Ammoniacal $AgNO_3$ soln. reduced to metallic Ag by soln. of guaiacol in NaOH.

Anisyl alcohol, $C_6H_4 \begin{smallmatrix} \text{OCH}_3 \\ \text{CH}_2\text{OH} \end{smallmatrix} \begin{smallmatrix} (1) \\ (2) \end{smallmatrix}$, m.p. 25°.

Salicylic aldehyde, $C_6H_4 \begin{smallmatrix} \text{OH} \\ \text{CHO} \end{smallmatrix} \begin{smallmatrix} (1) \\ (2) \end{smallmatrix}$, b.p. 196°. Oil with aromatic odour (meadow-sweet). $FeCl_3$ gives deep violet colour to its sols. S.G. 1.172 @ 13° C.

Anisic aldehyde, $C_6H_4 \begin{smallmatrix} \text{OCH}_3 \\ \text{CHO} \end{smallmatrix}$, b.p. 248°. S.G. 1.126.

Protocatechuic aldehyde, $C_6H_3 \begin{smallmatrix} \text{OH} \\ \text{OH} \\ \text{CHO} \end{smallmatrix} \begin{smallmatrix} (1) \\ (3) \\ (4) \end{smallmatrix}$, b.p. 150°.

$FeCl_3$ gives deep green to aq. soln.

Vanillin, $C_6H_3 \begin{smallmatrix} \text{CHO} \\ \text{OCH}_3 \\ \text{OH} \end{smallmatrix} \begin{smallmatrix} (1) \\ (3) \\ (4) \end{smallmatrix}$, m.p. 80–81°. Fused with

KOH yields protocatechuic acid, $CH_3 \begin{smallmatrix} \text{OH} \\ \text{OH} \\ \text{COOH} \end{smallmatrix}$, which

gives green coloration with $FeCl_3$ soln.

Creosol, $C_6H_3.CH_3.OCH_3.OH$.

Eugenol, $C_6H_3 \begin{smallmatrix} \text{CH} = \text{CH}_2 \\ \text{OCH}_3 \\ \text{OH} \end{smallmatrix} \begin{smallmatrix} (1) \\ (3) \\ (4) \end{smallmatrix}$, b.p. 247°. Oil with

characteristic clove-like odour.

(1) FeCl_3 gives a blue coloration to its sols.

(2) Fused with KOH yields acetic and protocatechuic acids.

Piperonal, $\text{C}_6\text{H}_5\text{O}_2\text{CH}_2\text{CHO}$, m.p. 37° (artificial heliotrope perfume). Forms a well-crystallized compound with NaHSO_3 .

6. ALCOHOLS will have been indicated by V. 6, and solubility in water.

Methyl alcohol, CH_3OH , b.p. 66° . S.G. 0.797 @ $\frac{15^\circ}{15^\circ}$.

Colourless liquid, miscible with water.

- (1) Digest 1 to 2 c.c. of methyl alcohol under reflux with 20 c.c. of 10 % chromic acid soln. till oxidation complete ; distil over 10 c.c. and test distillate for formic acid (which see).
- (2) To 1 c.c. methyl alcohol add 1 gram NaCl and 2 c.c. H_2SO_4 , gently warm : methyl chloride is produced, which has a pleasant smell, and can be burnt at the mouth of the test-tube, giving a green-coloured flame.

Ethyl alcohol, $\text{C}_2\text{H}_5\text{OH}$, b.p. 78.4° . S.G. 0.7938 @ $\frac{15.6^\circ}{15.6^\circ}$.

Colourless liquid, miscible with water.

- (1) To 10 c.c. of strong soln. $\text{K}_2\text{Cr}_2\text{O}_7$ and 2 c.c. strong conc. H_2SO_4 , after warming, add 4 or 5 drops of alcohol : the odour of aldehyde is produced, and soln. turns green if sufficient alcohol be added. The aldehyde may be detected by passing into AgNO_3 soln. (Tollen's reaction) or Schiff's reagent.
- (2) To 0.5 c.c. alcohol add 5 c.c. of 10% soln. Na_2CO_3 , then add soln. of I in KI till soln. is yellow ; gently warm by placing t.t. in a beaker of hot water : the odour of iodoform is at once observed, and after a time yellow crys. of iodoform settle out.
- (3) Mix 0.5 c.c. of alcohol with 0.5 gram of fused sodium acetate and 2 c.c. of conc. H_2SO_4 ; gently warm ; a strong odour resembling that of apples is observed due to formation of ethyl acetate.

n-Propyl alcohol, $\text{C}_3\text{H}_7\text{OH}$, b.p. 97.4° . S.G. 0.8044 @ 20° .
Liquid with agreeable smell, miscible with water ; insol. in saturated soln. CaCl_2 .

Isopropyl alcohol, $\text{CH}_3\text{CH.OH.CH}_3$, b.p. 82.7° . S.G. 0.7887
@ 20° .

Isobutyl alcohol $(\text{CH}_3)_2\text{CH.CH}_2\text{OH}$, b.p. 108.4° . S.G. 0.802
@ 20° .

Amyl alcohol (of fermentation), b.p. $129-132^\circ$. S.G. 0.8113
@ 18.7° . Liquid with disagreeable odour ; lævo-rotatory ;
consists of—

(a) Isobutyl carbinol, $(\text{CH}_3)_2\text{CH.CH}_2\text{CH}_2\text{OH}$.

(b) Secondary butyl carbinol, $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{OH}$.
[α] $_d = -52^\circ$.

(i.) Easily oxidized by alk. KMnO_4 to valeric acid, with
characteristic odour.

(ii.) Heated with fused sodium acetate and H_2SO_4
yields amyl acetate, which has characteristic odour.

Allyl alcohol, $\text{CH}_2\text{CH.CH}_2\text{OH}$, b.p. $96-97^\circ$. S.G. 0.854
@ 20° . Liquid with characteristic pungent odour ; easily
miscible with water.

(1) To 2 c.c. of aqueous soln. add ammoniacal AgNO_3
soln. : powerful odour of acrolein obtained.

(2) Oxidized by chromic acid to formic acid (apply test
as for methyl alcohol).

(3) Br water is instantly decolorized.

Glycol, $\text{C}_2\text{H}_4(\text{OH})_2$, b.p. 197.7° . S.G. 1.125 @ 0° . Liquid
miscible with water and alcohol.

Glycerine, $\text{C}_3\text{H}_8(\text{OH})_3$, b.p. 290° . S.G. 1.265 @ 15° . A thick,
colourless, syrupy liquid, miscible with water.

(1) Heat 0.5 c.c. with 1 to 2 grams KHSO_4 : acrolein
produced, detected by irritating odour.

(2) To 5 c.c. of aqueous soln. of glycerine add am-
moniacal soln. of AgNO_3 : a deposit of Ag is
obtained, and a mirror of Ag, if tube is clean.

(3) To 5 c.c. of soln. of glycerine add 5 c.c. of weak soln.
of borax, and then a few drops of alcoholic phenol-
phthalein ; a colourless solution is obtained, which
becomes red on warming, and colourless again on
cooling.

Benzyl alcohol, $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$, b.p. 206° . S.G. 1.062 @ 0° .
Colourless liquid, with faint aromatic odour ; sparingly sol.
in water, readily sol. in alcohol and ether.

Oxidize 0.5 c.c. with alk. KMnO_4 : benzoic acid is
produced, which can be liberated from the soln. of
potassium benzoate formed in solution.

Borneol, $C_{10}H_{17}OH$, m.p. 206–207 (sublimes), alcoholic soln. $[\alpha]_D + 33^\circ$. Insol. in water, sol. in alcohol, ether, and petroleum spirit. Bornylacetate, m.p. 29° .

Terpineol, $C_{10}H_{17}OH$, b.p. 218° – 219° . S.G. 0.940. Insol. in water, sol. in alcohol, ether, hydrocarbons, and fatty oils.

Terpin hydrate, $C_{10}H_{18}(OH)_2 \cdot H_2O$, m.p. 116° – 117° . Sol. in cold, and readily sol. in hot water. When heated to melting point loses water, leaving Terpin as a vitreous mass.

Menthol, $C_{10}H_{19}OH$, m.p. 42° – 43° (volatile). Sol. in alcohol, ether, carbon bisulphide, and fixed volatile oils; insol. in alkalies; solution in 5% alcohol @ 22° C. $[\alpha]_D - 49.4^\circ$. Forms an acetate when heated with $(CH_3CO.O)_2O + CH_3CO.ONa$.

- (i.) Form benzoyl ester with C_6H_5COCl ; separate and det. m.p. or b.p. (see IX. 2).
- (ii.) Oxidize with chromic acid (see VI. 4) and examine products of oxidation, viz. aldehydes or ketones and acids.

7. ETHERS. Indifferent bodies, and identified by b.p.

- (i.) Oxidation with chromic acid yields same products as corresponding alcohol.
- (ii.) PCl_5 converts them into alkylgen.

ETHER, $(C_2H_5)_2O$, b.p. 35° . S.G. 0.736 @ 0° . Mobile liquid with characteristic odour, slightly sol. in water, miscible with alcohol.

8. CARBOHYDRATES. Test V. 3 and 3a will have given indications of this group.

(I) MOLISCH'S REACTION FOR CARBOHYDRATES.

—To 2 c.c. of a 0.1% soln. of the substance in water add 2 drops of a 20% alcoholic soln. of α -naphthol, and then carefully pour 2 c.c. of conc. H_2SO_4 down the side of the test-tube: a deep violet coloration is produced, which gradually spreads throughout the liquid; this colour is discharged by KOH soln.

(2) FENTON'S REACTION FOR CARBOHYDRATES.¹—

A minute quantity of the solid is moistened with water ; mixed with 1 to 2 drops of PBr_3 dissolved in C_2H_5 , and gradually heated in the water bath to 90° – 100° till mixture turns dark coloured. Then cooled and stirred with a little $\text{C}_2\text{H}_5\text{OH}$ and a few drops of $\text{CH}_2(\text{CO}.\text{OC}_2\text{H}_5)_2$ and finally made alkaline with alcoholic KOH ; on diluting with a large quantity of water a *blue fluorescence* is obtained. Action due to formation of ω bromo-ethyl-furfuraldehyde. All Hexoses or compounds which yield Hexoses give the reaction.

Test systematically for—

- A. Glucoses. (a) Pentoses, *e.g.* arabinose, xylose, and rhamnose.
 (b) Hexoses. (i.) Aldoses, *e.g.* glucose, galactose, mannose.
 (ii.) Ketoses, *e.g.* fructose.
 B. Disaccharides, *e.g.* saccharose (cane-sugar), lactose, and maltose.
 C. Polysaccharides, *e.g.* starches, dextrine, and cellulose.

(3) TO DISTINGUISH BETWEEN PENTOSES AND HEXOSES.—

Distil 1 to 2 grams of substance with 10 c.c. of water and 5 c.c. conc. HCl ; collect 5 c.c. of distillate and test several portions as follows for furfural ($\text{C}_4\text{H}_3\text{O}.\text{CHO}$) :—

- (a) Add a few drops of aniline and conc. HCl : a deep red coloration is produced.
 (b) Carry out Molisch's reaction (given by furfural). Furfural is produced in the above reaction by action of HCl on the Pentoses.

(4) REACTION TO DISTINGUISH BETWEEN KETOSES AND ALDOSES.—

- (a) Method of Berg (*Bull. Soc. Chim.*, 1904, (iii.) 31, 1216). Heat 0.5 gram of the sugar with 10 c.c.

¹ *J.C.S.*, 1907, A. ii. 308.

of Br water for 10 mins. to a temp. of 60–70° C. ; boil off excess of Br ; then add about 1 c.c. of a 4% soln. of FeCl_3 and 1 drop of HCl. A deep yellow coloration shows the presence of hydroxy acids, produced by the oxidation of an *aldose*.

- (i.) Given by glucose, galactose, arabinose, and xylose.
- (ii.) Not given by *lævulose* or sorbose.
- (b) Method of Fenton (B.A. 1904, p. 513). Solns. of keto-hexoses, when oxidized by H_2O_2 in presence of a trace of FeSO_4 at 90–100°, and the resulting soln. heated with phenylhydrazine p.-sulphonic acid, produce a pinkish-brown soln. which dyes silk a rich brownish-pink colour. Given also by substances which yield keto-hexoses on hydrolysis.
 - (i.) *Lævulose*, cane-sugar, inulin, and sorbose give it readily.
 - (ii.) Dextrose, milk-sugar, maltose, or starch only slightly or not at all.

(5) IDENTIFICATION BY MEANS OF FORMATION OF OSAZONE.—

Dissolve 1 gram of the sugar in 20 c.c. of water in a large test-tube ; add 2.5 grams of phenylhydrazine and 3 c.c. of glacial acetic acid ; loosely stopper the tube and place in a beaker of boiling water ; shake from time to time. Yellow crystals of the osazone will settle out in from 10 to 15 minutes.¹ Filter, wash with water, dry, and determine m.p. (N.B.—The osazone may be further purified by crystallization from soln. in hot aniline, filtered, washed with dilute acetic acid, then water, etc.)

The osazones can be readily identified under the microscope. Draw up into a dropping-tube about 1 c.c. of the liquid together with the osazone as first precipitated, place 2 or 3 drops of this liquid on a microscope slide, cover with a cover-glass and

¹ Glucose, under conditions given, yields its osazone in the time stated, but the other sugars require a longer time to give precipitates of their osazones.

examine with the microscope, using a 1-inch objective and No. 1 eye-piece. Each osazone has a distinct crystalline form which is readily recognized. (See Figs. 13-22, which are photographic reproductions of osazones obtained and examined as described.)

(6) THE OPTICAL ACTIVITY of a solution of the carbohydrate may be determined as a confirmatory test.

- (a) Make, accurately, 50 c.c. of a soln. containing from 2.5 to 5 grams of the substance; boil for 2 to 3 minutes, and cool to room temperature. (Some sugars show multirotation, and boiling destroys this property and bestows constant rotation.)
- (b) Use a 10 or 20 cm. polarizing tube according to the activity of the soln.
- (c) A sodium flame is used for half-shadow polarimeters, and ordinary gaslight for neutral-tint polarimeters; whichever is used, ascertain the zero of the instrument by filling the polarizing tube with distilled water and taking an observation. Then take observation with prepared solution.
- (d) If α = the observed angular rotation, c = no. of grams of substance per 100 c.c. of volume, and l = length of polarizing tube in decimetres, then the specific rotatory power $[\alpha]$ for sodium light is given by $[\alpha]_D = \frac{100\alpha}{l \times c}$.

The following table gives the more important constants and special reactions:—

Glucose, $\text{CH}_2\text{OH}(\text{CHOH})_4\text{CHO}$, m.p. 144–146°. A white crys. solid, easily sol. in water, difficultly sol. in alcohol.

- (i.) $[\alpha]_D = 52.7$ for 10 % sol.
- (ii.) Osazone: yellow crys., m.p. 204–205°.
- (iii.) Reduces Fehling's on warming.
- (iv.) Conc. H_2SO_4 added to solid gives no colour in cold, but on prolonged heating turns brown.
- (v.) To 5 c.c. of glucose soln. add 5 drops of CuSO_4 soln. and excess of KOH soln.: no ppt. is produced, but on warming, a yellow, and finally a red, ppt. of Cu_2O is thrown down.

Galactose, $\text{CH}_2\text{OH}(\text{CHOH})_4\text{CHO}$, m.p. $163-164^\circ$.

- (i.) $[\alpha]_D = 83.8$.
- (ii.) Osazone: yellow crys., m.p. $204-205^\circ$.
- (iii.) Reduces Fehling's on warming.
- (iv.) Produces a pentacetate on warming with $(\text{CH}_3\text{CO}_2)_2\text{O}$ and ZnCl_2 (fused); m.p. 142° .

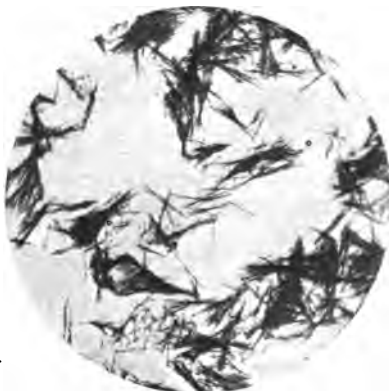


FIG. 13.—Glucose-osazone $\times 25$.

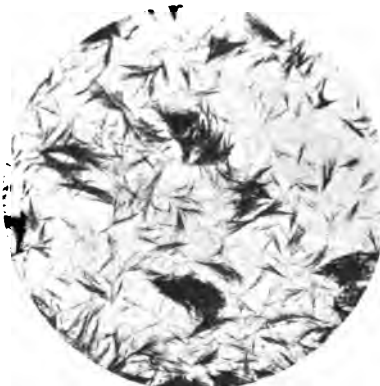


FIG. 14.—Fructose-osazone $\times 25$.

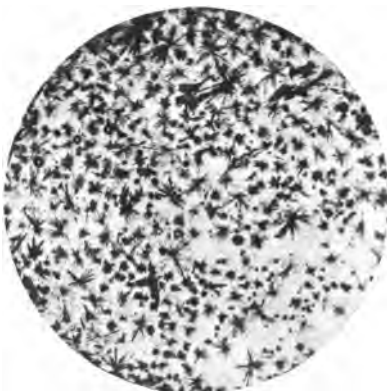


FIG. 15.—Maltose-osazone $\times 25$.

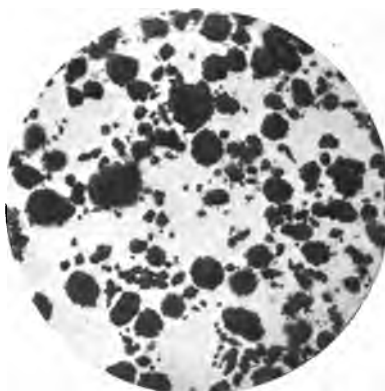


FIG. 16.—Lactose-osazone $\times 25$.

Mannose, $\text{CH}_2\text{OH}(\text{CH.OH})_4\text{CHO}$, m.p. 136° .

- (i.) $[\alpha]_D = 13$.
- (ii.) Osazone: yellow crys., m.p. $204-205^\circ$.
- (iii.) Reduces Fehling's on warming.

Fructose, $\text{CH}_2\text{OH}(\text{CH.OH})_3\text{CO.CH}_2\text{OH}$, m.p. 95° .

- (i.) $[\alpha]_D = - [102 - 0.56t]$.
- (ii.) Osazone: yellow crys., m.p. $204-205^\circ$.
- (iii.) Reduces Fehling's on warming.



FIG. 17.—Galactose-osazone $\times 25$.



FIG. 18.—Arabinose-osazone $\times 25$.



FIG. 19.—Xylose-osazone $\times 25$.

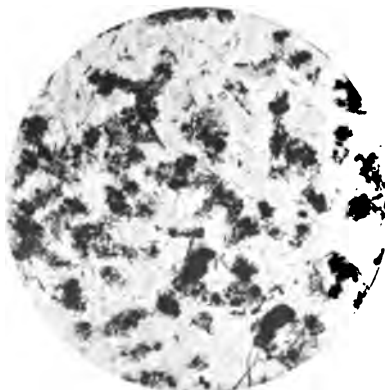


FIG. 20.—Mannose-osazone $\times 25$.

Saccharose (cane-sugar), $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, m.p. 160° . A crys. solid, easily sol. in water, difficultly sol. in alcohol.

- (i.) $[\alpha]_D = 66.5$ at 20° ; after boiling a soln. with dil. HCl $[\alpha]_D = - [27.9 - 0.32t]$ due to formation of fructose and dextrose (invert sugar).

- (ii.) Does not form an osazone.
- (iii.) Does not reduce Fehling's ; after boiling with dil. acids it reduces Fehling's.

Lactose, $C_{12}H_{22}O_{11} + H_2O$, m.p. 203.5° to a brown liquid ; insol. in alcohol.

- (i.) $[\alpha]_D = 52.5$.
- (ii.) Osazone : yellow crys., m.p. 200° .
- (iii.) Reduces Fehling's on *boiling*.
- (iv.) 0.5 gram of sugar heated with dil. HNO_3 in an evap. basin till red fumes cease to be evolved, then 1 or 2 c.c. more acid added and whole evaporated to dryness, a white powder of mucic acid left, difficultly sol. in water (not produced by glucose, saccharose, or dextrine).



FIG. 21.—Mannose-osazone $\times 25$.

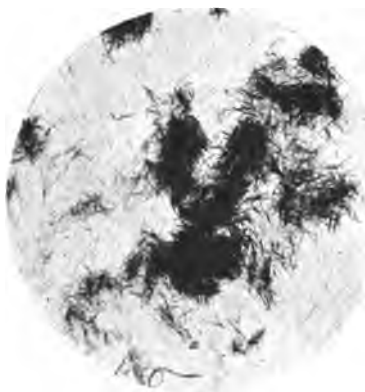


FIG. 22.—Rhamnose-osazone $\times 25$.

Maltose, $C_{12}H_{22}O_{11} + H_2O$.

- (i.) $[\alpha]_D = 138$.
- (ii.) Osazone : yellow crys., m.p. $190-191^\circ$.
- (iii.) Reduces Fehling's on *boiling*.

Arabinose, $CH_2OH(CHOH)_3CHO$, m.p. 100° ; slightly sol. in water.

- (i.) $[\alpha]_D = 104.5$.
- (ii.) Osazone : yellow crys., m.p. 160° .
- (iii.) Reduces Fehling's on warming.

Xylose, $CH_2OH(CH_2OH)_3CHO$, m.p. $144-145^\circ$.

- (i.) $[\alpha]_D = 18$.
- (ii.) Osazone : yellow crys., m.p. 160° .
- (iii.) Reduces Fehling's on warming.

Rhamnose, $\text{CH}_3(\text{CH.OH})_4\text{CHO}$, m.p. 93° .

(i.) $[\alpha]_D = 9$.

(ii.) Osazone : yellow crys., m.p. 180° .

(iii.) Reduces Fehling's.

Raffinose, $\text{C}_{18}\text{H}_{32}\text{O}_{16} \cdot 5\text{H}_{20}$ more sol. in water than cane sugar.

(i.) $[\alpha]_D = 104^\circ$.

(ii.) Does not reduce Fehling's solution.

Starch $(\text{C}_6\text{H}_{10}\text{O}_5)_n$. A white powdery solid, insol. in cold water, alcohol, and ether; soluble on boiling in water, and remaining in solution on cooling.

(i.) To 5 c.c. of a weak soln. of starch add 4 or 5 drops of a soln. of I in KI: a deep blue coloration produced; on heating the blue colour is discharged, and reappears on cooling.

(ii.) Fehling's soln. is not reduced by starch solns.; but is if starch be hydrolyzed to other carbohydrate, viz.—

1. Boil 0.5 gram starch with 10 c.c. water and 1 c.c. conc. HCl for 10 mins.; neutralize and add Fehling's; warm: a red ppt. of Cu_2O produced due to presence of glucose and dextrine.

2. To 5 c.c. of starch soln. add 1 c.c. of fresh malt extract, and heat for 5 mins. at 65° : on adding Fehling's, red Cu_2O is pptd. due to presence of maltose and dextrine.

Dextrine, $(\text{C}_6\text{H}_{10}\text{O}_5)_n$. A white to yellow powder, sol. in cold water and dilute alcohol; *insol. in abs. alcohol*.

(i.) I in KI produces a red coloration in dextrine solns. if dextrine obtained from starch by heat, acids, or alkalies; but only a yellow color. of I if made from starch by diastase.

(ii.) Fehling's soln. is not reduced until soln. of dextrine has been hydrolyzed by dil. HCl.

(iii.) $[\alpha]_D = 200.4$.

Cellulose $(\text{C}_6\text{H}_{10}\text{O}_5)_n$. A white, amorphous solid, insol. in water, alcohol, ether, etc.; soluble in an ammoniacal copper soln. (copper hydrate dissolved in ammonium hydrate); repptd. on adding HCl.

9. ESTERS AND GLUCOSIDES. Digest 2 grams or c.c. of substance with 50 c.c. of 10% KOH soln. under reflux till ester, etc., has disappeared; distil over two-thirds of the liquid and proceed as follows:—

Distillate test for alcohol by (a) oxidn. to aldehyde, etc.; (b) with C_6H_5COCl , etc.

Residue in flask dilute with water and filter if necessary. Test one portion of solution for glucose; if present = glucoside. If glucoside absent, test for acid obtained from the ester, which if insoluble in water can be pptd. by acidifying with HCl , and then identified as in 1.

The eqt. of the ester can be determined by digesting 1 gram with 50 c.c. $N.NaOH$ (alc.), and titrating excess of $NaOH$ after hydrolysis with $\frac{N}{10} H_2SO_4$ (and phenolphthalein).

If glucoside present, the following may be tested for :—

1. Salicine, m.p. $201^\circ C$. $C_6H_4 \begin{matrix} O.C_6H_{11}O_5(1) \\ \text{CH}_2OH(2) \end{matrix}$ Bitter taste.

(a) Conc. H_2SO_4 produces a red coloration.

(b) Take 0.15 gram KOH and 0.5 c.c. H_2O in a crucible and heat till KOH dissolved; add 0.5 gram of substance, and gently heat till mass just solidifies; cool, boil with water, and filter. Test filtrate after neutralizing for salicylic acid by adding few drops of $FeCl_3$ soln. : deep violet coloration.

(c) When hydrolyzed by dil. H_2SO_4 , products are glucose and saliretan—a condensation product of saligenin—which settles out as a whitish-yellow powder on cooling. Oxidizing this product (add $K_2Cr_2O_7$ soln., and conc. H_2SO_4 to liquid after boiling c. dil. H_2SO_4), and distilling over about 2 c.c. of the liquid, salicylic aldehyde will be found in the distillate, which is recognized by its aromatic odour and deep violet coloration produced with $FeCl_3$ soln.

2. Populin, $C_6H_4 \begin{matrix} O.C_6H_{11}O_5(1) \\ CH_2.OC_7H_5O(2) \end{matrix}$, m.p. 180° . Sweet; difficultly sol. in water,

(a) Hydrolyzed by dil. HCl products are C_6H_5CHO (and $C_6H_5CO_2H$), $C_6H_{12}O_6$, and saliretan. Hence test for C_6H_5CHO .

(b) Treated as 1 (b), salicylic acid can be identified in products.

3. **Helicin**, $C_6H_4 \begin{smallmatrix} O.C_6H_{11}O_6(1) \\ CHO(2) \end{smallmatrix}$, m.p. 175°.

Hydrolyzed with HCl yields $C_6H_4 \begin{smallmatrix} OH \\ CHO \end{smallmatrix}$ and $C_6H_{12}O_6$, which may be tested for after hydrolysis.

4. **Amygdalin**, $C_{20}H_{27}NO_{11}$, m.p. 200°. Sol. in water and alcohol; insol. in ether.

Hydrolyzed with dil. H_2SO_4 produces C_6H_5CHO , $C_6H_{12}O_6$, and HCN, which is evolved.

5. **Arbutin**, $C_6H_4 \begin{smallmatrix} O.C_6H_{11}O_6(1) \\ OH(4) \end{smallmatrix}$, m.p. 187°. Sol. in water.

(a) $FeCl_3$ gives deep blue colour to its soln.

(b) Hydrolyzed with dil. H_2SO_4 yields $C_6H_4(OH)_2$ (1.4) and $C_6H_{12}O_6$. Hence test for these.

The following are some of the more important esters:—

Ethyl formate, $H.CO_2.C_2H_5$, b.p. 54.5° (rum-like odour). S.G. 0.9445.

Isoamyl formate, $H.CO_2.C_5H_{11}$, b.p. 123° (fruity odour).

Methyl acetate, $CH_3.CO_2.CH_3$, b.p. 57.5°. S.G. 0.9577 @ 0°.

Ethyl acetate, $CH_3.CO_2.C_2H_5$, b.p. 77° (apple-like odour). S.G. 0.9238 @ 0°.

Amyl acetate, $CH_3.CO_2.C_5H_{11}$, b.p. 140° (pear-like odour).

Isoamyl propionate, $C_2H_5.CO_2.C_5H_{11}$, b.p. 160° (pine-apple odour).

Ethyl butyrate, $C_3H_7.CO_2.C_2H_5$, b.p. 121° (pine-apple odour).

Isoamyl butyrate, $C_3H_7.CO_2.C_5H_{11}$, b.p. 178° (pear-like odour).

Isoamyl-isovalerate, $C_4H_9.CO_2.C_5H_{11}$, b.p. 196° (apple odour).

Spermaceti (cetyl palmitate), $C_{15}H_{31}.CO_2.C_{16}H_{33}$, m.p. 49°.

Chinese wax (ceryl cerotate), $C_{26}H_{53}.CO_2.C_{27}H_{55}$.

Myricyl palmitate, $C_{16}H_{33}.CO_2.C_{30}H_{61}$ (constituent of beeswax).

Methyl oxalate, $(CO_2.CH_3)_2$, m.p. 51°. Sol. in water to $H_2C_2O_4$ and CH_3OH .

Ethyl oxalate, $(CO_2.C_2H_5)_2$, b.p. 186°. Slowly sol. in water. S.G. 1.0793 @ 20°.

Ethyl malonate, $CH_2(CO_2.C_2H_5)_2$, b.p. 195°. S.G. 1.068 @ 18°.

Ethyl tartrate, $(CH.OH.CO_2.C_2H_5)_2$, b.p. 280°. [α]_D +.

Ethyl benzoate, $C_6H_5.CO_2.C_2H_5$, b.p. 213°.

Benzyl benzoate, $C_6H_5.CO_2.CH_2C_6H_5$, m.p. 21° (occurs in tolu balsam).

Methyl salicylate, $C_6H_4 \begin{smallmatrix} OH \\ CO_2CH_3 \end{smallmatrix}$, b.p. 224° (chief ingred. of oil of wintergreen). S.G. 1.197 @ 0°.

Phenyl salicylate (salol), $C_6H_4 \begin{smallmatrix} OH \\ CO_2.C_6H_5 \end{smallmatrix}$, m.p. 43°.

Benzyl cinnamate, $C_6H_5 \cdot CH:CH \cdot CO_2 \cdot C_7H_7$, m.p. 39° (aromatic odour).

Cinnamyl cinnamate, $C_6H_5 \cdot CH:CH \cdot CO_2 \cdot C_9H_9$, m.p. 44° (aromatic odour).

Benzyl acetate, $C_6H_5 \cdot CH_2 \cdot CO_2 \cdot CH_3$, b.p. 206° .

Methyl anthranilate, $C_6H_4 \cdot NH_2 \cdot CO \cdot OCH_3$, m.p. 25° . S.G. 1.168.

Bornyl acetate, $C_{10}H_{17} \cdot CO_2 \cdot CH_3$, m.p. 29° . S.G. 0.991.

Menthyl acetate, $C_{10}H_{17} \cdot CO_2 \cdot CH_3$, b.p. 223° .

Geranyl acetate, $C_{10}H_{17} \cdot CO_2 \cdot CH_3$, b.p. $242^\circ-245^\circ$. S.G. 0.9174.

Geranyl tiglate, $C_{10}H_{17} \cdot CO_2 \cdot C_4H_7$.

Aceto-acetic ester, $CH_3 \cdot CO \cdot CH_2 \cdot CO_2 \cdot C_2H_5$, b.p. 180.8° . S.G. 1.0526 @ 20° .

(i.) $FeCl_3$ soln. produces violet colour with the ester.

(ii.) Boiled with KOH decomposed into $(CH_3)_2CO$, C_2H_5OH and CO_2 .

X. CARBON, HYDROGEN, AND NITROGEN PRESENT.

Indicates Amines (or salts of HCl , HBr , HI , H_2SO_4 , HNO_3 , or H_3PO_4), Hydrazines (or salts), Alkaloids (or salts), Cyanides (HCN and its salts; Ferro- and Ferri-cyanides), and Isocyanides. Pyridine and Quinoline. Pyrrol group. Azo-compounds and isomeric Benzidine and Tolidines (or their salts).

(a) Test IV. will have indicated a *metallic* derivative; if so, test for metallic cyanide, ferrocyanide, or ferri-cyanide (see end of X. A.).

(b) To a little of the substance add dilute HCl (1 to 10).

(i.) Immediately dissolves = amine, alkaloid, hydrazine, pyridine and quinoline, or pyrrol (slowly dissolves), benzidine or tolidine.

(ii.) Insoluble or very slowly sol. = cyanide, isocyanide or an azo-compound.

[If substance is a salt of amine, etc., it will be soluble in water, and test V. 1 will have indicated.]

A. INSOLUBLE IN DILUTE HCl. Ethereal smell = cyanide ; disgusting odour = isocyanide ; intensely coloured substance = azo-compound.

1. HEAT 1 to 2 c.c. under reflux with 20 c.c. conc. HCl till substance completely decomposed. Make alkaline with NaOH soln. and heat.

(i.) Alkaline vapours evolved may be—

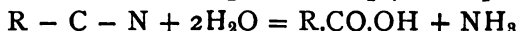
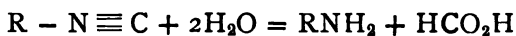
(a) NH_3 from a cyanide.

(b) Amine from an isocyanide ; recognized as in X. 3 (i.) (a), (b) ; if latter, it may be collected in dil. HCl, the PtCl_4 salt formed and mol. wt. determined.

(ii.) Test liquid remaining in flask for—

(a) Sodium formate = isocyanide ;

(b) Sodium salt of other organic acids = cyanide.



2. MIX 1 c.c. of substance with 10 c.c. of dil. HCl (1 to 3), add Zn dust and digest at a gentle heat for a few minutes, the cyanides and azo-compounds are converted into amines, which may be isolated and identified as in X. 3 (i.) (a) (b). (Na and absolute alcohol can be used instead of Zn, etc., in order to reduce the cyanides to amines.)

3. Test specially for—

Acetonitrile, CH_3CN , b.p. 81.6° . Colourless liquid with an agreeable smell. Miscible with water.

1. Reaction A. 1 produces acetic acid and ammonia, which test for.

2. Reaction A. 2 produces ethylamine hydrochloride, which test for.

Propionitrile, $\text{C}_2\text{H}_5\text{CN}$, b.p. 98° . S.G. 0.787.

Butyronitrile, $\text{C}_3\text{H}_7\text{CN}$, b.p. 118° (odour of bitter almonds).

Azo-benzene, $\text{C}_6\text{H}_5\text{N} = \text{N.C}_6\text{H}_5$, m.p. 68° . An orange-red crys. solid, easily sol. in alcohol and ether, sparingly sol. in water.

1. Reduced by Zn dust and NaOH to hydrazobenzene (colourless), a body possessing a camphor-like odour.
2. Reduced by Zn dust and HCl (prolonged action) to aniline, which test for.

p-Amido-azo-benzene, $C_6H_5.N_2.C_6H_4.NH_2$, yellow needles or prisms, m.p. 123° .

Diamido-azo-benzene, $C_6H_5.N_2.C_6H_3(NH_2)_2$, " " " m.p. 117° . Its HCl salt is named Chrysoidine.

Hydrazobenzene, $C_6H_5.NH.NH.C_6H_5$, colourless plates, m.p. 131° (odour of camphor).

Ferrocyanides.

1. Heated with conc. H_2SO_4 solid ferrocyanides evolve CO.
2. Sols. of ferrocyanides heated with dilute H_2SO_4 evolve HCN.
3. To soln. of ferrocyanide add a few drops of $FeCl_3$: a deep blue ppt. of Prussian blue obtained, insol. in HCl, decomposed by NaOH to ferric hydrate and sodium ferrocyanide.

Ferricyanides.

- 1 and 2. Reactions similar to ferrocyanide.
3. $FeCl_3$ no ppt., but soln. slightly darkens.
4. $FeSO_4$ soln. gives a deep blue ppt. of Turnbull's blue.

Note.—The double cyanides of the heavy metals are decomposed by—

1. Boiling NaOH, yielding a soln. of $Na_4FeC_6N_6$ and a ppt. of the hydrate of the metal.
2. Boiling conc. H_2SO_4 , evolving HCN and forming sulphates of the metal, Fe and NH_4 .

Cyanides (metallic).

1. Heated with dil. H_2SO_4 evolves HCN, which has characteristic odour, and is extremely poisonous.
2. Add dil. H_2SO_4 to 0.1 to 0.2 gram of a cyanide in a crucible, and instantly cover with an inverted watch-glass which has been moistened with a drop of yellow ammonium sulphide; warm gently; remove the watch-glass and add to it a drop of $FeCl_3$ and a drop of HCl: a blood-red colour produced owing to formation of ammonium sulphocyanide from the HCN and yellow Am_2S (*excess of Am_2S must be expelled before adding $FeCl_3$ soln.*).
3. To a soln. of the cyanide add a little NaOH soln. and 1 to 2 c.c. of saturated $FeSO_4$ soln.; well boil; then add 1 drop of $FeCl_3$ and enough conc. HCl to make the soln. acid: Prussian blue is formed, which turns soln. blue or may be pptd.

B. SOLUBLE IN DILUTE HCl. Proceed as follows:—

3. AMINES.

(i.) Mix 0.1 gram of substance with 3 drops CHCl_3 and 2 c.c. alcoholic potash, and gently warm: disgusting odour due to a carbylamine indicates a primary amine¹ (mono or di-²; fatty or aromatic). To distinguish between fatty and aromatic, dissolve 0.1 gram of substance in excess of dil. HCl; cool thoroughly and add a solution of KNO_2 or NaNO_2 till excess of free HNO_2 is obtained (place drop of diazotized soln. in a soln. of starch and KI). Divide into two portions —

(a) Heat one portion: N is evolved, and

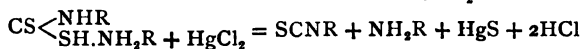
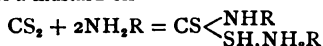
(a) An alcohol produced = fatty amine.

(β) A phenol „ = aromatic amine.

(b) To other portion add a soln. of α or β naphthol in NaOH, when an intensely coloured ppt. will be obtained if an aromatic primary, mono- or diamine or benzidine and tolidine.

(ii.) Secondary and tertiary. If primary absent, on adding NaNO_2 soln. to acid soln. of body, a yellow ppt. or soln. is obtained of a nitroso-compound if amine is secondary or tertiary. This may be separated and confirmed by Liebermann's nitroso reaction. (Meta-diamines yield yellow to yellowish-brown sols. or ppts. of an azo dye.)

¹ Confirm primary amine by Hofmann's mustard-oil reaction:—Digest 0.1 gram of substance with 1 c.c. CS_2 and 1 c.c. of HgCl_2 soln.: a characteristic odour is produced, due to formation of a mustard oil—



Some di-amines do not give this reaction readily.

- (iii.) To distinguish secondary from tertiary.
- Mix 1 c.c. of substance with 1 c.c. CH_3I and gently warm : a crys. mass of an amm. iodide will be formed if tertiary.
 - Mix 1 c.c. of substance with 1 c.c. CH_3COCl or $\text{C}_6\text{H}_5\text{COCl}$ (and NaOH) : an anilide is produced if secondary. (Primary also produce anilide.)
- (iv.) If amine cannot be identified, its eqt. wt. should be det. from PtCl_4 compound.

The following amines may be specially tested for :—

Methylamine, CH_3NH_2 . A gas with characteristic odour, easily sol. in water. It forms a well-crystallized salt with HCl , viz. $\text{CH}_3\text{NH}_2\cdot\text{HCl}$, m.p. 210° .

(1) The salts of CH_3NH_2 are decomposed on warming with NaOH , evolving CH_3NH_2 as a gas.

(2) The salts give the characteristic reaction of amines (see above).

(3) Soln. of $\text{CH}_3\text{NH}_2\cdot\text{HCl}$ added to a soln. of picric acid gives a ppt. of methyl ammonium picrate.

Ethylamine, $\text{C}_2\text{H}_5\text{NH}_2$, liquid, b.p. 18° ; S.G. 0.696 @ 8° . Forms well-crystallized salt with HCl , viz. $\text{C}_2\text{H}_5\text{NH}_2\cdot\text{HCl}$, m.p. $76-80^\circ\text{C}$.

Trimethylamine, $(\text{CH}_3)_3\text{N}$. A compound, liquid below 3.5° , having a very penetrating fish-like smell; forms a salt with HCl , viz. $(\text{CH}_3)_3\text{N}\cdot\text{HCl}$, m.p. $271-275^\circ$; the picrate, m.p. 216° . Sparingly sol. in water.

Tetramethylammonium Salts, $(\text{CH}_3)_4\text{NX}$, are well crystallized salts, soluble in water; on adding moist Ag_2O to their solns., they produce insol. AgI and a strongly alkaline solution of tetramethylammonium hydroxide.

(a) $(\text{CH}_3)_4\text{NI}$. White crys. solid, sol. in water or alcohol.

(b) $(\text{CH}_3)_4\text{N.OH}$. Deliquescent crys. solid, sol. in water to a strongly alkaline soln.

Aniline, $\text{C}_6\text{H}_5\text{NH}_2$, b.p. 184° ; S.G. 1.036 @ 0° . Colourless oily liquid, turning brown on exposure to air and light; sparingly sol. in water, readily sol. in alcohol and ether; forms well-crystallized salts with acids.

1. To weak soln. of aniline add a filtered soln. of bleaching powder, drop by drop : a purple coloration produced, gradually changing brown ; on adding a drop of ammonium sulphide to the purple soln. a rose-coloured soln. is obtained.
2. To 1 c.c. of aniline add a few drops of conc. H_2SO_4 and a few drops of K_2CrO_4 : a red colour is produced, which changes to an intense blue.

Toluidine (ortho), b.p. 199° ; S.G. = 1.00 @ 16° ; o- acet-toluide, m.p. 110° .

(i.) Bleaching powder and HCl colour it violet.

(ii.) FeCl_3 ppts. a blue compound from its soln. in HCl.

(para), m.p. 45° ; p- acet-toluide, m.p. 153° .

Methyl-aniline, $\text{C}_6\text{H}_5\text{NHCH}_3$, b.p. $190-191^\circ$; S.G. 0.976 @ 15° . Salts sol. in water and ether.

Dimethyl-aniline, $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$, b.p. 192° ; S.G. 0.955 .

Its nitroso derivative gives a yellow-colored soln. in HCl, and is pptd. from acid solns by alkalies as a greenish solid.

Diphenylamine, $(\text{C}_6\text{H}_5)_2\text{NH}$, m.p. 54° . Insol. in water ; easily sol. in alcohol and ether ; dissolves easily in H_2SO_4 , and in presence of trace of HNO_3 gives a dark blue colour.

α -Naphthylamine, $\text{C}_{10}\text{H}_7\text{NH}_2$, m.p. 50° . Colourless crys. solid, turning red on exposure to the air, and easily sublimes, producing pungent odour.

Soln. of its hydrochloride in water gives blue ppt. with FeCl_3 .

β -Naphthylamine, $\text{C}_{10}\text{H}_7\text{NH}_2$, m.p. 112° . Colourless solid, odourless.

FeCl_3 produces no colour change.

3a. DIAMINES.

- (i.) Digest 0.5 gram of substance with 5 c.c. of 10% FeCl_3 soln.—

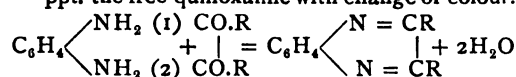
(a) Red-coloured soln. indicates an ortho- or meta- diamine.

(b) Odour of quinone produced is a para-diamine ; confirm by gently heating with MnO_2 and H_2SO_4 , which oxidize p-diamines to quinone;

- (ii.) Dissolve 0.1 gram of substance in 1 c.c. alcohol and add a few drops of a hot acetic acid soln. of phenanthraquinone: a yellow ppt. of a quinoxaline produced = an ortho-diamine (Hinsberg).

The quinoxalines are—

- (a) Well-crys. yellow or orange substances, with high b.p. and sublime below b.p. to voluminous flakes
- (b) Form salts with all mineral acids (red or orange).
- (c) Dissolve in excess of conc. H_2SO_4 , with characteristic colours, which, on adding to water, ppt. the free quinoxaline with change of colour.



- (iii.) Digest 0.1 gram of substance with 0.5 gram of NH_4CNS ; add a soln. of $\text{Pb}(\text{OH})_2$ in NaOH , warm: a black ppt. obtained indicates—

- (a) a meta-diamine;
- (b) a para-diamine.

- (iv.) To 0.1 gram of substance add 5 c.c. SH_2 soln., then 1 c.c. conc. HCl , and finally a few drops of FeCl_3 soln.; an intense colour will be produced if a para-compound (blue to violet). [Lauth's dye-stuffs.]

The following are the more important with additional characteristic reactions:—

- A. o-Phenylenediamine, $\text{C}_6\text{H}_4(\text{NH}_2)_2$, m.p. 102° . Colourless solid, easily sol. in hot water, alcohol, and ether.
- m-Phenylenediamine, $\text{C}_6\text{H}_4(\text{NH}_2)_2$, m.p. 63° . Crys. solid, slightly sol. in water, very sol. in alcohol and ether.

When its aqueous soln. is added to a very dil. soln. of HNO_3 , it gives a yellow to brown soln. due to formation of Bismarck brown, $(\text{NH}_2)_2\text{C}_6\text{H}_3-\text{N}=\text{N}-\text{C}_6\text{H}_4\text{NH}_2$.

- p-Phenylenediamine, $\text{C}_6\text{H}_4(\text{NH}_2)_2$, m.p. 147° . Crys. solid; slightly sol. in water, very sol. in alcohol and ether.

(i.) Mixed with phenol and oxidized in alkaline soln. with NaClO produces a violet coloration due to formation of indophenol, $N \begin{array}{c} \text{C}_6\text{H}_4\cdot\text{NH}_2 \\ \text{C}_6\text{H}_4\text{O} \end{array}$ (Witt).

(ii.) Using aniline instead of phenol yields a greenish-blue colour (phenylene blue), due to formation of indoamine, $N \begin{array}{c} \text{C}_6\text{H}_4\cdot\text{NH}_2 \\ \text{C}_6\text{H}_4\cdot\text{NH} \end{array}$ (Witt).

(See below for further reactions.)

m-p-Diamidotoluene, $\text{C}_6\text{H}_3\text{CH}_3(\text{NH}_2)_2$ (1.3.4.), m.p. 89° .

p-Dimethylphenylenediamine, $\text{C}_6\text{H}_4 \begin{array}{c} \text{N}(\text{CH}_3)_2 \\ \text{NH}_2 \end{array}$ (1) m.p.

41°. Crys. solid, easily sol. in water, alcohol, and ether.

Yields methylene blue with the SH_2 and FeCl_3 reaction, viz. $(\text{CH}_3)_2\text{N}\cdot\text{C}_6\text{H}_3\text{N}\cdot\text{C}_6\text{H}_3(\text{CH}_3)_2\text{Cl}$.

B. Benzidine, $\text{NH}_2\cdot\text{C}_6\text{H}_4\text{—C}_6\text{H}_4\cdot\text{NH}_2$, m.p. 122° . Colourless crystalline laminæ when pure, becoming reddish-brown by oxidation; sparingly sol. in cold water, easily in hot.

(1) To cold saturated soln. add H_2SO_4 : a white ppt. of benzidine sulphate obtained.

(2) To diazotized soln. of benzidine add an alkaline soln. of naphthionic acid: Congo red is produced.

o-Tolidine, $\begin{array}{c} \text{NH}_2 \\ \text{CH}_3 \end{array} > \text{C}_6\text{H}_3\text{—C}_6\text{H}_3 < \begin{array}{c} \text{NH}_2 \\ \text{CH}_3 \end{array}$ (1.3.4.). Crys. laminæ, m.p. 128° .

The following amino-compounds are those commonly used as developing agents in photography: ¹—

1. p-Amido-phenol hydrochloride, $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2\cdot\text{HCl}$. A crys. solid; m.p. of base, 184°C . The salt decomposes on heating. The salt is easily sol. in water, difficultly sol. in alcohol and ether; the base is easily sol. in hot water, sparingly sol. in alcohol, difficultly sol. in ether.

(i.) Conc. HCl ppts. the salt from its aqueous soln.

(ii.) Very easily oxidized to quinone by acid dichromate, FeCl_3 soln., or MnO_2 and H_2SO_4 .

(iii.) Bleaching powder soln. added to an aqueous soln. of the salt containing a little free HCl, produces a violet-coloured soln., which, with excess of B.P. soln., gives a yellow flocculent ppt. of quinone chlorimide.

¹ See "Photographische Correspondenz," etc. Wien, 1898.

- (iv.) On diazotizing and coupling with an alkaline soln. of Andressen's¹ α -naphthol disulphonic acid, a ponceau-red azo-compound is produced.
2. Methyl-p-amido-phenol sulphate (metol), $(\text{HO.C}_6\text{H}_4.\text{NH.CH}_3)_2\text{H}_2\text{SO}_4$. Needle-shaped crys. solid; m.p. of base, 87°C . The salt decomposes on heating without melting; the salt is easily sol. in water, sparingly sol. in alcohol and ether; the free base easily sol. in alcohol and ether, sparingly sol. in water.
- (i.) Easily oxidized to quinone.
- (ii.) A soln. of salt in dil. H_2SO_4 gives, on adding KNO_3 , after a time, a ppt. of matted needles, consisting of the nitroso-derivative, $\text{HO.C}_6\text{H}_4.\text{N.NO.CH}_3$.
3. Methyl-o-amido-phenol sulphate, $(\text{HO.C}_6\text{H}_4.\text{NH.CH}_3)_2\text{H}_2\text{SO}_4$. Mixed with hydroquinone it appears as the developer ortol. Crystalline plates; m.p. of base, 80°C ; salt decomposes on heating without melting; easily sol. in water, sparingly sol. in alcohol and ether.
- Oxidation of a soln. of salt with acid dichromate produces a deep Bordeaux-red coloured soln.; ortol under the same conditions also yields quinone from oxidation of the hydroquinone.
4. p-Phenylene-diamine hydrochloride, $\text{C}_6\text{H}_4(\text{NH}_2)_2.2\text{HCl}$. A crys. solid; m.p. of base, 147°C . The salt decomposes on heating without melting; the salt is easily sol. in water; the base easily sol. in alcohol and ether, slightly sol. in water.
- (i.) Conc. HCl ppts. the salt from its aqueous soln.
- (ii.) Oxidation with acid dichromate easily yields quinone.
- (iii.) Bleaching-powder soln. yields a yellow flocculent ppt. of quinone-dichlor-diimide.
- (iv.) On diazotizing and coupling with Andressen's α -naphthol disulphonic acid, a red-violet azo-compound is produced.
5. 2,4 Diamido-phenol hydrochloride (amidol), $\text{C}_6\text{H}_3\text{OH}(\text{NH}_2)_2.2\text{HCl}$ (1.2.4.). Needle-shaped crys. solid; easily sol. in water, sparingly sol. in alcohol and ether; decomposed on heating without melting.
- (i.) Conc. HCl ppts. the salt from its aqueous soln.
- (ii.) A soln. of salt in Na_2SO_3 soln. produces—
- (a) With K_2CO_3 soln. a blue colour.
- (b) With KOH soln. a Bordeaux-red colour.
- (iii.) FeCl_3 soln. gives, with aqueous soln. of the salt, an intense red coloration.
6. Diamido-resorcin hydrochloride, $\text{C}_6\text{H}_2(\text{OH})_2(\text{NH}_2)_2.2\text{HCl}$ (1.3.4.6.). Rhombic crys. solid; very easily sol. in water,

¹ Andressen's acid is $\text{C}_{10}\text{H}_7.\text{OH}.\text{SO}_2\text{H}.\text{SO}_2\text{H}$ (1.3.8.).

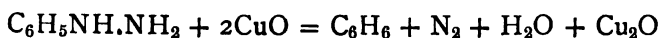
sparingly sol. in alcohol and ether; decomposed on heating without melting.

- (i.) Conc. HCl ppts. the salt from its aqueous soln.
 - (ii.) A soln. of salt in Na_2SO_3 soln. produces—
 - (a) With K_2CO_3 soln., a yellowish-brown colour.
 - (b) With KOH soln., a blue colour.
 - (iii.) 1 or 2 drops of FeCl_3 soln. added to a strong aqueous soln. of the salt produces an intense violet coloration, which disappears after a short time.
7. Diamido-oxy-diphenyl, $\begin{matrix} (4) \text{HO} \\ (1) \text{NH}_2 \end{matrix} > \text{C}_6\text{H}_4 - \text{C}_6\text{H}_4 \cdot \text{NH}_2$ (3), m.p. 148°C . Crystallizes from water in matted needles. Easily sol. in alcohol, cold acetic acid, and hot water; sparingly sol. in benzene; and almost insol. in cold water.
- (i.) Insol. in solns. of Na_2SO_3 or Na_2CO_3 ; sol. in solns. of NaOH or KOH.
 - (ii.) On diazotizing and coupling up with Andressen's α -naphtho-disulphonic acid gives a ponceau-red coloured azol compound.
8. Triamido-phenol hydrochloride, $\text{C}_6\text{H}_3(\text{OH})(\text{NH}_2)_3 \cdot 3\text{HCl}$ (1.2.4.6). Needle-shaped crys. solid; decomposed on heating without melting; easily sol. in water, difficultly sol. in alcohol and ether.
- (i.) Conc. HCl ppts. the salt from its aqueous soln.
 - (ii.) In an aqueous soln. —
 - (a) Na_2SO_3 soln. produces a yellow coloration.
 - (b) K_2CO_3 soln. produces a green coloration.
 - (c) KOH soln. produces a brown coloration.
 - (iii.) 1 or 2 drops of FeCl_3 soln. to a weak soln. of the salt yields a deep blue colour, but no quinone.
9. α_1 -Amido- β_1 -naphthol- β_2 -sulphonic acid, $\text{C}_{10}\text{H}_7 \cdot \text{NH}_2 \cdot \text{OH} \cdot \text{SO}_3\text{Na}$ (Eikonogen). Rhombic crys. plates. Easily sol. in hot, slightly sol. in cold water; almost insol. in alcohol and ether. The crystals lose water of crystallization at 110°C .
- (i.) Acids ppt. the free acid from solution of its sodium salt as white needle crystals.
 - (ii.) KOH or NaOH soln., added to aqueous soln. of salt, produces a fine golden-yellow coloration.
10. p-Oxy-phenyl-glycin (glycin), $\text{HO} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2 \cdot \text{COOH}$. Mica-like crys. plates; sparingly sol. in water and alcohol, insol. in ether.
- (i.) Easily sol. in solns. of Na_2SO_3 , Na_2CO_3 , and NaOH.
 - (ii.) Aqueous soln. of its salts oxidized to quinone with evolution of CO_2 .

4. HYDRAZINES. Test for specially as follows:—

- (i.) Boil a few drops with CuSO_4 soln.: red Cu_2O ppt.

and the corresponding hydrocarbon is formed with the evolution of N. (FeCl_3 acts similarly.)



- (ai.) Fehling's soln. is reduced immediately in the cold by primary hydrazines, but only on warming by secondary hydrazines. (RNR.NH_2 or RNH.NHR.)
- (ii.) Test specially for $\text{C}_6\text{H}_5\text{NH.NH}_2$ as follows : dissolve 0.5 gram glucose in 5 c.c. H_2O ; dissolve 1 gram of given substance in 1.5 c.c. glacial acetic acid and dilute with 5 c.c. H_2O ; mix the two sols. in a test-tube, loosely stoppered, and place on water-bath : yellow crystals of phenylglucosazone settle out. Separate, wash and dry, and take m.p. (205°C.).
- (iii.) Metallic Na added to 1 c.c. of liquid dissolves with evolution of H and the Na derivative settles out (R.N.Na.NH_2).

α Methyl-phenylhydrazine $\text{C}_6\text{H}_5\text{NH.NH.CH}_3$.

β " " $\text{C}_6\text{H}_5\text{N(CH}_3\text{).NH}_2$,
b.p. 227° .

Phenylhydrazine, $\text{C}_6\text{H}_5\text{NH.NH}_2$. Crys. solid, m.p. 23° .

Its hydrochloride is a well-crystallized solid.

Methylhydrazine, $\text{CH}_3\text{.NH.NH}_2$, b.p. 87° .

Ethylhydrazine, $\text{C}_2\text{H}_5\text{NH.NH}_2$, b.p. 100° .

5. ALKALOIDS. The commonest are conine and nicotine, and may be identified by their powerful odour.

- (i.) Conine (n-propyl piperidine), $\text{C}_8\text{H}_{17}\text{N}$, b.p. 167° – 168° , S.G. 0.886 @ 0° , $[\alpha]_D = 13.8^\circ$. Its hydrochloride has m.p. 217° . Forms a nitroso derivative with NaNO_2 , etc., and a benzoyl derivative with $\text{C}_6\text{H}_5\text{COCl}$, etc. On gently

heating conine or its salts with HNO_3 , a smell of butyric acid is evolved.

- (ii.) Nicotine, $\text{C}_{10}\text{H}_{14}\text{N}_2$, b.p. 241° . S.G. 1.011 @ 15° .
Sol. in water to an alkaline soln.

To soln. of nicotine in water add excess of a saturated soln. of picric acid : an amorphous yellow ppt. is obtained, which readily changes to a mass of crystalline tufts.

6. PYRIDINE AND QUINOLINE.

- (i.) Pyridine,¹ $\text{C}_5\text{H}_5\text{N}$, b.p. 114.8° C. S.G. 1.003 @ 0° . Its hydrochloride forms rather insoluble double salt with PtCl_4 .

- (ii.) Quinoline, $\text{C}_9\text{H}_7\text{N}$, b.p. 239° C. S.G. 1.095 @ 0° .
Its hydrochloride readily crystallizes. Mixed with CH_3I forms crys. yellow compound m.p. 72° C. The hydrochloride mixed with $\text{K}_2\text{Cr}_2\text{O}_7$ soln. gives characteristic yellow crys. from hot sols., m.p. 165° .

- (iii.) Sols. of these two substances in HCl give the usual reactions for alkaloids (see XI. 13).

7. PYRROL AND ITS ALKYL derivatives.

Pyrrol reaction (Neuberg, *Chem. Centr.*, 1904, ii. 1435).

This reaction given by four classes of substances.

- (i.) Those giving it directly, *e.g.* pyrrol, indole, carbazole,
- (ii.) N containing substances which, when decomposed by heating, give off vapours capable of showing the reaction ; *e.g.* certain amino-acids and ammonium salts, as glutamic acid, ammonium malate, and ammonium pyruvate.
- (iii.) N containing substances which yield the reaction when heated with Zn dust, *viz.* glucosamine, glucose oxime, and ammonium salts of gluconic, tartaric, oxalic, and malonic acids.

¹ Alkyl derivatives, *viz.* picolines, lutidines, and collidines (methyl and ethyl pyridines), are constituents of bone oil and coal tar.

(iv.) N free oxygen containing substances which give pyrrol when heated with NH_3 or ammonium salts, viz. γ -diketones.

- (1) Moisten a pine shaving with HCl and hold it in the vapour of the substance: a pale red colour is obtained, which becomes an intense carmine-red (pyrrol reaction).
- (2) To 1 c.c. conc. H_2SO_4 add 1 c.c. of substance and a trace of isatin or phenanthraquinone: an indigo-blue coloration is obtained.
- (3) Add 0.1 gram K to pyrrol: H is evolved, and a crys. mass of $\text{C}_4\text{H}_4\text{NK}$ is obtained.

Pyrrol, $\text{C}_4\text{H}_4\text{NH}$, b.p. 131° ; S.G. 0.9752 @ 1.25° . Colourless liquid with odour resembling chloroform.

Soln. of pyrrol in dil. acid evolves NH_3 on being heated and ppts. a red amorphous powder (pyrrol red).

Methylpyrrol, $\text{C}_4\text{H}_4\text{NCH}_3$, b.p. 113° ; S.G. 0.9203 @ 10° .

Ethylpyrrol, $\text{C}_4\text{H}_4\text{N.C}_2\text{H}_5$, b.p. 113° ; S.G. 0.9042 @ 10° .

XI. CARBON, HYDROGEN, NITROGEN, AND OXYGEN PRESENT.

Amides, Amino-acids (or salts); Nitro-compounds (nitrophenols, nitroacids, nitroaldehydes, and nitroamines); Ureas (or salts), Ureides, Urethanes, Uric Acid group; Cyanates and derivatives, Isocyanates and derivatives; Oximes; Hydrazones, Osazones, Semi-carbazones; Esters of Nitrous and Nitric Acids; Azo-compounds (dyes); Anilides (or homologues); Alkaloids (or salts).

A. Digest about 1 to 2 grams of substance with 50 c.c. of 10% NaOH soln. under reflux till no further change.

(i.) NH_3 or alkaline vapours evolved shows presence of

(a) Amides: residue in flask contains Na salt.

(b) (i.) Urea „ „ „ Na_2CO_3 .

- (ii.) Alkyl ureas: residue in flask contains Na_2CO_3 and an amine if non-volatile.
- (c) Ureides: residue in flask contains Na salt of acid of ureide and Na_2CO_3 .
- (d) Urethanes: residue in flask contains Na_2CO_3 and an alcohol.
- (e) Isocyanates: residue in flask contains Na_2CO_3 .
- (ii.) Substance is decomposed with or without soln.
 - (a) Anilides:¹ free aniline, or its homologues, is produced which can be extracted with ether, etc., and residue contains Na salt.
 - (b) Ester: distil over two-thirds of the liquid and test distillate for an alcohol; residue in flask contains NaNO_3 or NaNO_2 .

Special tests should now be applied for the group indicated, viz. 1-8; if no indications given, proceed systematically testing for other substances as in B. 9-14.

I. AMIDES.

- (i.) Mix with equal bulk of P_2O_5 in a dry t.t. and collect vapours given off on gently heating (nitrile), which may or may not condense (see tests of Nitriles). PCl_5 also produces a nitrile.
- (ii.) Gently boil 0.5 gram of substance with 10 c.c. H_2O and 0.5 gram HgO : a soluble Hg compound is produced, which may crystallize out on cooling.

$$2\text{CH}_3\text{CO.NH}_2 + \text{HgO} = (\text{CH}_3\text{CO.NH})_2\text{Hg} + \text{H}_2\text{O}.$$

Formamide, HCO.NH_2 , b.p. $192-195^\circ$. Colourless liquid, readily sol. in water and alcohol.

P_2O_5 evolves HCN . $\text{HCO.NH}_2 = \text{HCN} + \text{H}_2\text{O}$.

¹ Anilides are extremely difficult to hydrolyse by this method. If anilide suspected hydrolyse by W. H. Perkin's method, viz. heat with conc H_2SO_4 and absolute $\text{C}_2\text{H}_5\text{OH}$ when an ester is produced.

Acetamide, $\text{CH}_3\text{CO.NH}_2$, m.p. $82-83^\circ$. Crys. solid, soluble in water and alcohol.

(i.) P_2O_5 evolves CH_3CN .

(ii.) NaOH evolves NH_3 and gives a soln. of sodium acetate (which test for).

Oxamide, $(\text{CO.NH}_2)_2$. White crys. powder, decomposed on heating; insol. in water and alcohol.

(i.) P_2O_5 evolves C_2N_2 . $(\text{CONH}_2)_2 = \text{C}_2\text{N}_2 + 2\text{H}_2\text{O}$.

(ii.) NaOH evolves NH_3 and gives a soln. of sodium oxalate (which test for).

Succinamide, $\text{C}_2\text{H}_4\text{CO.NH}_2$. White crys. solid, decomposed on heating into succinimide; sol. in water.

Benzamide, $\text{C}_6\text{H}_5\text{CO.NH}_2$, m.p. 130° . White crys. solid, sol. in hot water, alcohol, and ether.

- (iii.) The equivalent wt. of the amide can be determined as follows: Heat about 1 gram of the amide with 50 c.c. of N.NaOH in an apparatus for estimating NH_3 by distillation; collect the NH_3 evolved in 50 c.c. of $\text{N.H}_2\text{SO}_4$, and titrate excess of H_2SO_4 with $\frac{\text{N}}{10}\text{NaOH}$, using phenolphthalein.

2. AMINO-ACIDS. Generally sol. in water to a neutral soln.; insol. in alcohol and ether.

The more common are—

(1) Glycocoll, $\text{CH}_2\text{NH}_2\text{CO.OH}$, m.p. $232-236^\circ$.

(i.) KNO_3 and HCl produce glycollic acid and evolves N .

(ii.) FeCl_3 produces intense red coloration with solution; discharged by acids.

(2) Alanine, m.p. 255° (chars at 237°), $\text{CH}_3\text{CH.NH}_2\text{CO.OH}$.

(i.) KNO_3 and HCl produce α -lactic acid and evolve N .

(ii.) Heated with soda-lime evolves $\text{C}_2\text{H}_5\text{OH}$ and NH_3 .

(iii.) Heated with CaO yields $\text{C}_2\text{H}_5\text{NH}_2$.

(3) α -Amido-caproic acid, Leucine, $\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$, m.p. 170° . Sol. in water.

Fused with KOH it yields ammonium and potassium valerates.

- (4) Aspartic acid, $\text{CH}_3\text{NH}_2\text{CO.OH}$. HNO_2 converts to malic acid (which test for). The natural acid $[\alpha]_D$ —.
- (5) Asparagine, $\text{CH}_3\text{NH}_2\text{CO.OH}$. HNO_2 converts to malic acid (which test for). Sol. in hot water and natural acid $[\alpha]_D$ —.
- (6) Anthranilic acid, $\text{C}_6\text{H}_4\text{.NH}_2$ CO.OH , m.p. 144°C .
 - (i.) KNO_2 and HCl on warming yields salicylic acid (which test for).
 - (ii.) Heated with soda-lime yields $\text{C}_6\text{H}_5\text{OH}$ and NH_3 .
 - (iii.) Heated with CaO yields $\text{C}_6\text{H}_5\text{NH}_2$.
- (7) Hippuric acid, $\text{CH}_2\text{.NH.CO.C}_6\text{H}_5$ CO.OH , m.p. 187° .
 Digest 0.5 gram with 10 c.c. conc. HCl under reflux for 15 minutes. Cool, filter off crystals of benzoic acid (test these), neutralize filtrate with NH_4OH , boil off excess of NH_3 , and add CuSO_4 : a deep blue colour due to copper glyccoll.
- (8) Betaine, $\text{CH}_2\text{.N(CH}_3)_3\text{OH}$ CO.OH .
 - (i.) Heated alone gives $\text{N(CH}_3)_3$ and odour of burnt sugar.
 - (ii.) Fusion with KOH yields $\text{N(CH}_3)_3$.
 - (iii.) I in KI gives brown ppt. of periodide.

3. UREAS.

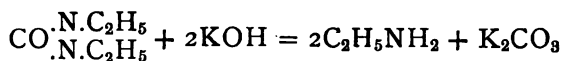
(i.) Apply usual tests for urea.

Urea, $\text{CO} < \begin{smallmatrix} \text{NH}_2 \\ \text{NH}_2 \end{smallmatrix}$. White crys. solid, m.p. 132° ; very sol. in water and alcohol, almost insol. in ether.

- (i.) Heated in a dry state, it melts and evolves NH_3 , and gives a white sublimate of ammonium cyanurate; residue gives bi-uret test.
- (ii.) To 3 c.c. of a strong soln. of urea in a watch-glass add 1 c.c. conc. HNO_3 : a crys. ppt. of urea nitrate is formed, which arranges itself in rosettes of needle-shaped crystals if soln. is not too strong.
- (iii.) Urea oxalate is also pptd. from strong solns. of urea and oxalic acid.

- (a) Urea nitrate, $\text{CO}(\text{NH}_2)_2 \cdot \text{HNO}_3$. Slightly sol. in water; when heated evolves pungent, disagreeable odour, somewhat like SO_2 .
- (b) Urea oxalate, $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{C}_2\text{O}_4 + \text{H}_2\text{O}$. Sol. in water.

(ii.) Alkyl ureas, when digested with KOH , are decomposed primarily into CO_2 and amines, viz.—



Hence test for carbonate in residue and for amine in distillate (if volatile); if non-volatile, test for amine in residue.

Methyl urea, $\text{CO} < \begin{smallmatrix} \text{NHCH}_3 \\ \text{NH}_2 \end{smallmatrix}$, m.p. 102° .

Ethyl urea, $\text{CO} < \begin{smallmatrix} \text{NH} \cdot \text{C}_2\text{H}_5 \\ \text{NH}_2 \end{smallmatrix}$, m.p. 109° .

α -Diethyl urea, $\text{CO} < \begin{smallmatrix} \text{NH} \cdot \text{C}_2\text{H}_5 \\ \text{NH} \cdot \text{C}_2\text{H}_5 \end{smallmatrix}$, m.p. 112° .

Diallyl urea, $\text{CO} < \begin{smallmatrix} \text{NH} \cdot \text{C}_3\text{H}_5 \\ \text{NH} \cdot \text{C}_3\text{H}_5 \end{smallmatrix}$, m.p. 100° .

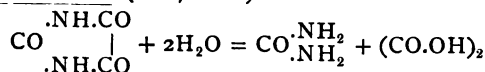
Phenyl urea, $\text{CO} < \begin{smallmatrix} \text{NHC}_6\text{H}_5 \\ \text{NH}_2 \end{smallmatrix}$, m.p. 144° .

Diphenyl urea, $\text{CO} < \begin{smallmatrix} \text{NH} \cdot \text{C}_6\text{H}_5 \\ \text{NH} \cdot \text{C}_6\text{H}_5 \end{smallmatrix}$, m.p. 235° .

4. UREIDES.

These, when heated with KOH , are decomposed into urea and an acid [the urea is further decomposed as in 3 (ii.)], hence test for a carbonate and the K salt of the acid produced by hydrolysis, *e.g.*—

Parabanic acid (oxalyl urea)

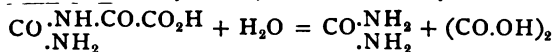


(i.) Sol. in water and alcohol, insol. in ether.

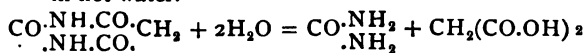
(ii.) AgNO_3 gives crys. ppt. of $\text{C}_3\text{Ag}_2\text{N}_2\text{O}_3$.

(iii.) A soln. of potassium ethylate added to an alcoholic soln. of the acid gives a crys. ppt. of the potassium acid parabanate $C_5H_7KN_2O_3$.

Oxaluric acid. Crys. solid, sol. with difficulty in water.



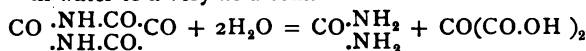
Malonyl urea (barbituric acid). White crys. solid, sol. in hot water.



(i.) $AgNO_3$ gives white ppt. of $Ag_2C_4H_2N_2O_3$ with ammoniacal soln. of the acid.

(ii.) KNO_3 soln. to soln. of acid gives a soln. of violuric acid, $C_4H_2(N \cdot OH)_2N_2O_3$, which gives a red ppt. with $BaCl_2$ soln. and a dark blue colour with $FeCl_3$ soln.

Mesoxalyl urea (alloxan). White crys. solid, easily sol. in water to a very acid soln.

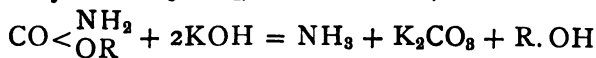


(i.) This substance in soln. gives an indigo-blue coloured soln. with $FeSO_4$ soln.

(ii.) To soln. add KCN soln., HCl , and then make alkaline with NH_4OH : a white ppt. of oxalureamide, $CO < \underset{NH_2}{NH} \cdot CO \cdot CO \cdot NH_2$, is obtained.

5. URETHANES, $CO < \underset{O \cdot R}{NH_2}$. These are crystalline solids very soluble in water, alcohol, and ether; on heating they volatilize.

(i.) Heated with KOH soln. as in XI. A, they yield NH_3 , CO_2 , and an alcohol, viz.



hence the residue in flask will contain K_2CO_3 and an alcohol, which should be tested for.

(ii.) Metallic Na added to an ethereal soln. of a urethane evolves H .

Methyl urethane, $CO < \underset{O \cdot CH_3}{NH_2}$, m.p. 52° .

Ethyl urethane (urethane), $\text{CO} < \begin{smallmatrix} \text{NH}_2 \\ \text{O.C}_2\text{H}_5 \end{smallmatrix}$, m.p. 47–50°.

Propyl urethane, $\text{CO} < \begin{smallmatrix} \text{NH}_2 \\ \text{O.C}_3\text{H}_7 \end{smallmatrix}$, m.p. 53°.

Isoamyl urethane, $\text{CO} < \begin{smallmatrix} \text{NH}_2 \\ \text{OC}_5\text{H}_{11} \end{smallmatrix}$, m.p. 60°.

Allyl urethane, $\text{CO} < \begin{smallmatrix} \text{NH}_2 \\ \text{OC}_3\text{H}_5 \end{smallmatrix}$, m.p. 21°, b.p. 204°.

URIC ACID GROUP.

These all give a characteristic reaction, viz. 0.1 gram substance is evaporated to dryness carefully with 5 c.c. Cl water: a yellow residue is obtained, which turns red on gently heating. Moisten this with NH_4OH (2 or 3 drops): a reddish-purple or purple colour is obtained.

Guanine, $\text{C}_5\text{H}_5\text{N}_5\text{O}$, amorphous powder, insoluble in H_2O , $\text{C}_2\text{H}_5\text{OH}$ and $(\text{C}_2\text{H}_5)_2\text{O}$.

- (1) To soln. in HCl add K_2CrO_4 soln.: an orange-coloured ppt. obtained.
- (2) To soln. in HCl add $\text{K}_4\text{FeC}_6\text{N}_6$ soln.: a brown-coloured ppt. obtained.
- (3) To soln. in HCl add saturated soln. of picric acid: an orange-yellow ppt. obtained.

Xanthine, $\text{C}_5\text{H}_4\text{N}_4\text{O}_2$; insol. in alcohol and ether.

- (1) To saturated aqueous ammoniacal solution add HgCl_2 solution: a white ppt.
- (2) To saturated aqueous ammoniacal solution add AgNO_3 solution: a white ppt. of $\text{C}_5\text{H}_2\text{Ag}_2\text{N}_4\text{O}_2 \cdot \text{H}_2\text{O}$.
- (3) To a mixture of bleaching-powder and NaOH solution in a watch-glass, add a small piece of solid: a dark green spot, changing to brown and then disappearing, obtained.

Uric Acid, $\text{C}_5\text{H}_4\text{N}_4\text{O}_3$. A white shining powder; very slightly soluble in water, insoluble in alcohol and ether; decomposed by heat into NH_3 , CO_2 , urea, and cyanuric acid.

- (1) Murexide test ; evaporate 0.1 gram with 2 c.c. HNO_3 carefully to dryness : an orange residue obtained, which is coloured violet-red by NH_4OH soln., and violet-blue by KOH soln.
- (2) Dissolved in Na_2CO_3 soln. and few drops placed on piece of paper moistened with AgNO_3 soln., produces dark brown spot.

Theobromine, $\text{C}_5\text{H}_2(\text{CH}_3)_2\text{N}_4\text{O}_2$. Crystalline powder slightly soluble in hot water, alcohol, and ether. Sublimes at about 290° .

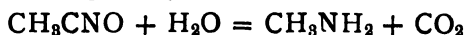
To saturated cold solution add ammoniacal solution of AgNO_3 : a gelatinous ppt. is formed, which dissolves on warming.

Caffeine, $\text{C}_8\text{H}_8(\text{CH}_3)_2\text{N}_4\text{O}_2$. Long silky needles, slightly soluble in cold water and alcohol, very slightly in ether ; loses H_2O at 100° , and melts at 233° .

- (1) Gives murexide test as uric acid.
- (2) Aqueous solution gives a yellow ppt. with a solution of phosphomolybdic acid.
- (3) Evaporate a soln. of Cl water, containing a trace of caffeine, to dryness : a reddish-brown spot obtained, turning violet-red with NH_4OH .

6. ISOCYANATES (metallic derivatives and esters).

Indicated by powerful odour. Heated with alkalis become primary amines.



Potassium Cyanate, $\text{KN}:\text{C}:\text{O}$. Crys. leaflets ; readily sol. in cold water, difficultly sol. in hot alcohol.

- (1) Unacted on by heat.
- (2) AgNO_3 soln. gives white ppt. of Ag salt, sol. in HNO_3 or NH_4OH .
- (3) $\text{Pb}(\text{NO}_3)_2$ soln. gives white ppt. of Pb salt.
- (4) Heated with Na as in Lassaigne's test yields Cyanamide.

Cyanuric Acid, $\text{H}_3\text{C}_3\text{O}_3\text{N}_3 \cdot 2\text{H}_2\text{O}$, rhombic prisms, sol. in water.

- (1) Heated with acids yields CO_2 and ammonium salt of the acid.
- (2) Heated alone yields cyanic acid.
- (3) Aqueous soln. heated with conc. NaOH yields minute needles of $\text{Na}_3\text{O}_3\text{N}_3\text{C}_3$.

7. ANILIDES (Acid).

Test A (ii.) (a) will have detected an anilide. It may be further identified by—

- (i.) Determining m.p.
- (ii.) Preparing a nitroso-derivative ($\text{HCl} + \text{NaNO}_2$ soln.).

Formanilide, $\text{C}_6\text{H}_5\text{NH.COH}$, m.p. 46° .

Acetanilide, $\text{C}_6\text{H}_5\text{NH.CO.CH}_3$, m.p. 112° . Sol. in boiling water.

Oxanilide, $(\text{C}_6\text{H}_5\text{NHCO})_2$, m.p. 245° .

Acet-o-toluide, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_3 \\ \text{NHCOCH}_3 \end{smallmatrix}$, m.p. 110° .

Acet-p-toluide, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_3 \\ \text{NH.COCH}_3 \end{smallmatrix}$, m.p. 147° .

Nitro-anilides should be specially looked for.

p. nitro-acetanilide, m.p. 207° , gives p. nitro-phenol when heated with strong KOH solution.

8. ESTERS OF NITROUS AND NITRIC ACIDS.

A (ii.) (b) will have detected these. Identify by—

- (i.) Determining b.p. of ester, or
- (ii.) Identifying the alcohol obtained on hydrolysis with alkalis.

Methyl nitrate, $\text{CH}_3\text{O.NO}_2$, b.p. 66° ; S.G. 1.182 @ 20° .

Ethyl nitrate, $\text{C}_2\text{H}_5\text{O.NO}_2$, b.p. 86° ; S.G. 1.112 @ 15°

Colourless, pleasant-smelling liquid; slightly sol. in water.

Ethyl nitrite, $\text{C}_2\text{H}_5\text{O.NO}$, b.p. 16° ; S.G. 0.947 @ 15° . Insol. in water; alcoholic soln. commonly used.

Isoamyl nitrite, $\text{C}_5\text{H}_{11}\text{O.NO}$, b.p. 96° ; S.G. 0.902. Yellow liquid.

B. 9. NITRO-COMPOUNDS.(1) A. Aromatic nitro-compounds.

- (i.) All insoluble in water or dilute HCl or dilute NaOH soln. Di- and tri-nitro compounds colour NaOH soln. a deep yellow.
- (ii.) Mix in test-tube 4 or 5 drops of nitro-compound, 1 c.c. of water, 2 c.c. conc. HCl, and add slowly about 1 gram Zn dust; warm if necessary. Dilute with 5 c.c. of water, and add strong NaOH till ppt. first formed is redissolved: an amine is produced, which may be separated either by funnel direct or extraction with ether, etc. The amine can be recognized by usual tests. Test specially for aniline by bleaching-powder test; this reaction given by fatty and aromatic nitro-compounds.



- (iii.) Dissolve 3 drops of a nitro-compound in 3 c.c. of 50 % alcohol. To this soln. add 6 drops of $CaCl_2$ soln. (1 to 10) and a pinch of Zn dust. Heat till solution boils, and after allowing to stand 5 minutes filter. To filtrate add strongly ammoniacal soln. of $AgNO_3$: a deposit of Ag obtained—



NOTE.—Do not apply this if original body reduces $AgNO_3$. Nitroso-, azo-, and azoxy-compounds give this reaction.

- (iv.) In this reaction the quantities must be taken fairly accurately. Dissolve 3 drops of a nitro-compound in 3 c.c. of a mixture of equal parts of aniline, o. toluidine, and p. toluidine. Add 2 c.c. water, 2 c.c. of HCl (sp. gr. 1.2), and 1 gram of Fe filings. Boil almost to dryness in a basin, treat with water, and then pour a little of the

dark-coloured solution into a test-tube half full of dilute acetic acid: magenta or fuchsine colour is produced.

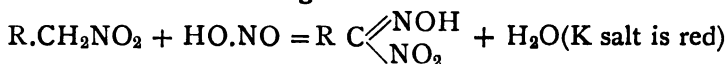
B. Fatty nitro-compounds. Agreeable odour; sparingly soluble in water, soluble in alkalies.

(i.) Dissolve 0.5 c.c. of substance in 5 c.c. strong KOH soln., add 2 c.c. KNO_2 soln., and then carefully add dil. H_2SO_4 .

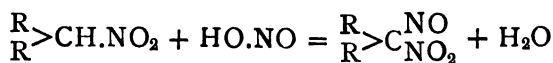
(a) Intense red coloration indicates primary nitro-compound.

(b) A dark blue coloration indicates secondary nitro compound.

(c) Tertiary nitro-compounds produce no change.



Nitrolic acid.



Pseudonitrol (blue).

(ii.) Reduced as in (2) above, yield amines.

Nitromethane, CH_3NO_2 , b.p. 101° .

(1) Add 1 c.c. of liquid to 5 c.c. of alc. NaOH soln.; a crys. ppt. of $\text{CH}_2\text{Na}(\text{NO}_2).\text{C}_2\text{H}_5\text{OH}$ obtained.

(2) Sols. of salts of heavy metals ppt. metallic compounds from its aqueous soln. of type $\text{CH}_2\text{M}(\text{NO}_2)$. (Note these are in many cases explosive).

Nitroethane, $\text{C}_2\text{H}_5\text{NO}_2$, b.p. $113-114^\circ$. S.G. 1.058 @ 13° .

(1) FeCl_3 gives a blood-red colour to aqueous soln. of its Na compound.

(2) CuSO_4 gives a dark-green colour to aqueous soln. of its Na compound.

α Nitropropane, $\text{CH}_3.\text{CH}_2.\text{CH}_2\text{NO}_2$, b.p. $125^\circ-127^\circ$.

Iso-nitropropane, $(\text{CH}_3)_2\text{CH}.\text{NO}_2$, b.p. 117° .

Tertiary nitrobutane, $(\text{CH}_3)_3\text{C}.\text{NO}_2$, b.p. 126° .

Nitrobenzene, $\text{C}_6\text{H}_5.\text{NO}_2$, b.p. 210° . S.G. 1.2 @ 0° .

Light yellow liquid with odour of bitter almonds;

very slightly sol. in water, readily sol. in alcohol, ether, benzene, and conc. HNO_3 .

- (1) Reduction with Zn and HCl gives aniline.
- (2) Warmed with conc. HNO_3 and H_2SO_4 and poured into water, it yields meta-dinitrobenzene, m.p. 89.9° .

m. Dinitrobenzene, $\text{C}_6\text{H}_4(\text{NO}_2)_2$. Colourless needle-shaped crys. solid, m.p. 89.9° .

o. Nitrotoluene, $\text{C}_6\text{H}_4\text{CH}_3\text{NO}_2$ (1), b.p. 218° . S.G. 1.163 @ 23° .

p. Nitrotoluene, $\text{C}_6\text{H}_4\text{CH}_3\text{NO}_2$ (4), m.p. 54° .

(2) Nitro-phenols.

- (a) Produce very soluble K and Na salts with NaOH and KOH, usually yellow to red in colour and decomposed by HCl; decompose alkaline carbonates.
- (b) Reduction with Sn and HCl produce amido-phenols, in which the amido group can be detected in usual manner.

Mononitrophenols, $\text{C}_6\text{H}_4\text{CH}_3\text{NO}_2$.

- (i.) Ortho-, m.p. 45° . Yellow crys.; peculiar odour; almost insol. in H_2O . Na salt dark red.
- (ii.) Meta-, m.p. 96° . Yellow crys.; moderately sol. in water.
- (iii.) Para-, m.p. 114° . Colorless crys.; sol. in water. K salt yellow.

Dinitrophenols.

- (i.) α . $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{OH}$ (1.3.4). Yellow plates, m.p. 114° .
- (ii.) β . $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{OH}$ (1.5.6). Yellow needles, m.p. 64° .

Trinitrophenols. Chief is picric acid, $\text{C}_6\text{H}_2(\text{OH})(\text{NO}_2)_3$ (1.2.4.6). A yellow crys. solid; slightly sol. in water to yellow soln. which stains silk or wool a deep yellow, m.p. 122.5° .

(See its compds. with Benzene, naphthalene, and anthracene.)

(3) Nitro-anilines.

(a) Yellow crys. solid. Det. m.p.

(b) Reduction with Sn and HCl produce diamines (see IX. 3 (a)).

o-Nitro-aniline, $C_6H_4 \begin{smallmatrix} \text{NH}_2 (1) \\ \text{NO}_2 (2) \end{smallmatrix}$, yellow needles, m.p. 71° .m-Nitro-aniline, $C_6H_4 \begin{smallmatrix} \text{NH}_2 (1) \\ \text{NO}_2 (3) \end{smallmatrix}$, m.p. 114° . Yellow crys. needles.p-Nitro-aniline, $C_6H_4 \begin{smallmatrix} \text{NH}_2 (1) \\ \text{NO}_2 (4) \end{smallmatrix}$, yellow needles, m.p. 147° .

These are easily decomposed by boiling with KOH into K salts of intropenols.

(4) Nitro-acids can be reduced by Sn and HCl, etc.o-Nitro-benzoic acid, $C_6H_4 \begin{smallmatrix} \text{CO}_2\text{H} (1) \\ \text{NO}_2 (2) \end{smallmatrix}$, m.p. 147.7° . Colourless crys. solid ; very slightly sol. in water, very sol. in alcohol and ether.m-Nitro-benzoic acid, $C_6H_4 \begin{smallmatrix} \text{CO}_2\text{H} (1) \\ \text{NO}_2 (3) \end{smallmatrix}$, m.p. 141° . White crys. solid ; slightly sol. in water ; sublimes.p-Nitro-benzoic acid, $C_6H_4 \begin{smallmatrix} \text{CO}_2\text{H} (1) \\ \text{NO}_2 (4) \end{smallmatrix}$, m.p. 238° . Yellowish crys. solid ; sol. in water, very sol. in alcohol and ether.Dinitro-benzoic acid, $C_6H_3\text{CO}_2\text{H}(\text{NO}_2)_2$ (1.3.5.), m.p. 204° .Nitro-phenylacetic acids, $C_6H_4(\text{NO}_2)\text{CH}_2\text{CO}_2\text{H}$.(i.) Ortho-, m.p. 141° . Crys. in needles from hot water.(ii.) Meta-, m.p. 120° .(iii.) Para-, m.p. 152° . Difficultly sol. in water.(5) Nitro-aldehydes possess the properties of aldehydes and nitro-compounds.Nitro-benzoic aldehydes, $C_6H_4 \begin{smallmatrix} \text{CHO} \\ \text{NO}_2 \end{smallmatrix}$.(i.) Ortho-, m.p. 44° . Yellow crys. solid ; slightly sol. in water, easily in alcohol.(ii.) Meta-, m.p. 58° . Crys. solid ; moderately sol. in water, easily in alcohol.(iii.) Para-, m.p. 156° . Colourless crys. ; slightly sol. in water, moderately in alcohol.

10. HYDRAZONES.

Those of aldehydes and ketones of fatty series mostly yellow oils; others, yellow or brown crys. solids. Those of hexoses colourless crys. solids, and are sol. in water.

- (i.) To 2 grams add 10 c.c. conc. HCl and digest under reflux till hydrolysis complete; cool and add NaOH soln. till strongly alkaline; $C_6H_5.NH.NH_2$ settles out and may be separated either by funnel or by extraction with ether, etc., and identified. The aqueous portion contains an aldehyde, ketone (if soluble), or glucose, which may be tested for.
- (ii.) Determine m.p. (This must be done rapidly, as they decompose on slowly heating.)
- (iii.) Try to prepare an osazone by adding to 0.5 gram of substance a soln. of $C_6H_5NH.NH_2$ in glacial acetic acid; separate the osazone which settles out, and det. m.p. Only those hydrazones derived from glucoses, α -diketones, α -alcohol-aldehydes, and α -keto-alcohols are capable of forming osazones.

Some of commonest hydrazones are—

Acetaldehyde hydrazone, m.p. 63–65°.

Acetone-phenylhydrazone, m.p. 16°, b.p. 165° (91 mm.).

Pyroracemic phenylhydrazone, $CH_3C(HN_2.C_6H_5)CO_2H$, m.p. 192°.

Lævulinic Phenylhydrazone, $CH_3.C(N.NH.C_6H_5).(CH_2)_2.CO_2H$, m.p. 108°.

Mannose phenylhydrazone, $C_6H_{12}O_5N.NHC_6H_5$, m.p. 195°.

α -Glucose phenylhydrazone, m.p. 145°.

β -Glucose phenylhydrazone, m.p. 116°.

Galactose phenylhydrazone, m.p. 158–160°.

Benzylidene-phenylhydrazone, $C_6H_5CH:N.NHC_6H_5$, m.p. 152.5°.

Acetol-hydrazone, $CH_3.C(N_2H.C_6H_5).CH_2OH$.

Acetophenone - phenylhydrazone, $\text{C}_6\text{H}_5 > \text{CN.NHC}_6\text{H}_5$,
 m.p. 105° .
 Diacetylhydrazone, $\text{CH}_3\text{C}(\text{N}_2\text{H.C}_6\text{H}_5)\text{CO.CH}_3$, m.p. 133° .
 Benzophenone - phenylhydrazone, $\text{C}_6\text{H}_5 > \text{C.N.NH.C}_6\text{H}_5$,
 m.p. 105° .
 Acetylacetone-hydrazone, $\text{CH}_3\text{C}(\text{N}_2\text{H.C}_6\text{H}_5)\text{CH}_2\text{CH}_2\text{CO.CH}_3$, m.p. 120° .
 Glyoxylic-hydrazone, $\text{CH}(\text{N}_2\text{H.C}_6\text{H}_5)\text{CO}_2\text{H}$.

11. OSAZONES.

Mostly yellow-coloured or bright red solids. Glucosazones, osazones of α -aldehyde alcohols, α -ketone alcohols, and α -diketones.

- (i.) Pechmann's reaction—Digest the substance with alcohol and FeCl_3 : a reddish-brown solution is produced, which is soluble in ether.
- (ii.) Digest in the cold 2 grams with conc. HCl till hydrolysis complete: $\text{C}_6\text{H}_5\text{NH.NH}_2$ and an osone is produced—

$\text{C}_6\text{H}_{10}\text{O}_4(\text{N}_2\text{H.C}_6\text{H}_5)_2 + \text{H}_2\text{O}$
 $= \text{CH}_2(\text{OH}).(\text{CH.OH})_3\text{CO.CHO} + 2\text{C}_6\text{H}_5\text{NH.NH}_2$
 Make strongly alkaline with NaOH , extract the $\text{C}_6\text{H}_5\text{NH.NH}_2$ liberated, and identify. Remaining solution divide into two parts—(1) Reduce with Zn dust, and after reduction test for a sugar (carbohydrate); and (2) add to soln. of 0.1 gram of o. $\text{C}_6\text{H}_4(\text{NH})_2$ in alcohol: a yellow ppt. of a quinoxalin indicates an ortho, dicarbonyl compound (*e.g.* an osone).

- (iii.) Mostly all soluble in cold conc. H_2SO_4 , giving coloured solutions which undergo change on standing.

See IX. 8 for list of osazones of sugars.

Glyoxal-osazone, $(\text{C}_6\text{H}_5\text{NH.N : CH})_2$, m.p. 177° .

$\text{CH}_3\text{C} = \text{N.NH.C}_6\text{H}_5$
 Diacetyl-osazone, $\text{CH}_3\text{C} = \text{N.NH.C}_6\text{H}_5$, m.p. 236° .

Acetol-osazone, $\text{CH}_3\text{C}(\text{N}_2\text{H.C}_6\text{H}_5)\text{CH}(\text{N}_2\text{H.C}_6\text{H}_5)$.

12. OXIMES (Aldoximes and Ketoximes). Colourless liquids or solids.

- (i.) Digest 2 grams with 10 c.c. conc. HCl under reflux ; hydrolyzed to NH_2OH salt and ketone or aldehyde.
 - (a) Test soln. for aldehyde or ketone.
 - (b) Evaporate to small bulk to expel aldehyde or ketone, redissolve $\text{NH}_2\text{OH.HCl}$ in water, and add AgNO_3 , which is reduced to Ag.
- (ii.) Treat 1 gram with 5 c.c. dilute acetic acid, 5 c.c. alcohol, and 1.0 gram of Na amalgam: an amine is produced which can be recognized by usual tests. The amine may, if necessary, be separated and identified by either determining mol. wt. by PtCl_4 salt, or its m.p. or b.p. determined.
- (iii.) Beckmann's reaction. Dissolve 1 gram in anhydrous alcohol free ether, and add gradually 1.5 grams PCl_5 ; distil off ether, add water, and crystallize the solid that settles out from alcohol. In this reaction substituted amides are produced, viz. $(\text{C}_6\text{H}_5)_2\text{C.NOH} = \text{C}_6\text{H}_5\text{NH.CO.C}_6\text{H}_5$. These are decomposed by boiling with alkalis into free amine and the Na salt of the acid, and these can be identified by usual method.

Acetaldoxime, $\text{CH}_3\text{.CH : NOH}$, m.p. 47° .

Chloraloxime, $\text{CCl}_3\text{.CH : NOH}$, m.p. $39-40^\circ$.

Acetoxime, $(\text{CH}_3)_2\text{C : NOH}$, m.p. $59-60^\circ$.

Glyoxime, $(\text{CH} = \text{NOH})_2$, m.p. 178° .

α -Benzaldoxime, $\text{C}_6\text{H}_5\text{.CH : NOH}$, m.p. 35° .

β -Benzaldoxime, $\text{C}_6\text{H}_5\text{.CH : NOH}$, m.p. 125° .

Acetophenoneoxime, $\text{C}_6\text{H}_5\text{.C : NOH.CH}_3$, m.p. 59° .

Diacetyl di-oxime, $(\text{CH}_3\text{C : NOH})_2$, m.p. 234° .

Acetonyl acetone dioxime, $(\text{CH}_3\text{C : NOH.CH}_2)_2$, m.p. 136° .

Furfuraldoxime, $\text{C}_4\text{H}_3\text{O.CH : NOH}$, m.p. 80° .

Quinine dioxime, $\text{HON : C}_6\text{H}_4 : \text{NOH}$.

Benzophenoxime, $(\text{C}_6\text{H}_5)_2\text{C : NOH}$, m.p. 140° .

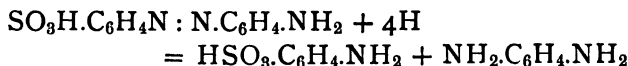
13. SEMI-CARBAZONES. Colourless crystalline solids derived from aldehydes and ketones.

The semi-carbazones are decomposed by dilute H_2SO_4 , regenerating the aldehyde or ketone. Heat 1 gram of semi-carbazone with a slight excess of dilute H_2SO_4 (15 per cent.) under a reflux till decomposed; distil off aldehyde or ketone with steam and test for same in the distillate. The residue in the flask contains hydrazine sulphate and semi-carbazide sulphate; hence test residue for hydrazine (see X. 4). The hydrazine sulphate can be recovered by concentration and crystallization¹:—

Aldehyde semi-carbazone,	$\text{CH}_3\text{CH} : \text{N.CO.NH.NH}_2$, m.p. 162° .
Acetone	" $(\text{CH}_3)_2\text{C} : \text{N.CO.NH.NH}_2$, m.p. 187° .
Acetophenone	" $(\text{C}_6\text{H}_5).\text{C}(\text{N.CO.NH.NH}_2).\text{CH}_3$, m.p. 198° .
Benzophenone	" $(\text{C}_6\text{H}_5)_2\text{C} : \text{N.CO.NH.NH}_2$, m.p. 164° .
Benzilmono	" $\text{C}_6\text{H}_5.\text{CO.C} : (\text{N.CO.NH.NH}_2).\text{C}_6\text{H}_5$, m.p. 174° .
Diacetyl-mono	" $\text{CH}_3.\text{CO.C} : (\text{N.CO.NH.NH}_2).\text{CH}_3$, m.p. 234° .

14. AZO-COMPOUNDS. (Oxy-, amido, and sulphonic derivatives.)

Digest 1 gram of substance with 20 c.c. of saturated soln. of SnCl_2 in HCl till compound completely reduced; add strong NaOH till $\text{Sn}(\text{OH})_2$ first pptd. is redissolved, when free amines will be liberated, and may be separated and identified, viz.—



If the azo-dye contains a sulphonic group, one of the products of reduction will always be an amino-sulphonic compound which is soluble in NaOH soln. After separating the free amines, either by steam distillation or extraction with ether, these sulphonic derivatives may be pptd. by carefully neutralizing the soln.

15. ALKALOIDS.

Easily soluble in dilute acids, repptd. by alkalis (morphine is soluble in excess of NaOH). The following reactions indicate an alkaloid:—

¹ *J.C.S.*, 1905, A. i. 179.

- (i.) Heated in dry t.t. give smell of burnt feathers.
- (ii.) Solutions of alkaloids give ppts. with following :—
 - (a) I in KI—dark yellowish - brown ppts. of periodide of alkaloid.
 - (b) Sodium phosphomolybdate soln.—yellowish-white ppt. (aniline, quinoline, salts of Ag, Hg, and Pb give ppt.).
 - (c) PtCl_4 —yellow or yellowish-white ppt. of double Pt salt.
 - (d) BiI_3 in KI—yellowish ppts.
 - (e) HgI_2 in KI—yellowish-white ppt.
 - (f) Tannic acid—white or yellowish-white clotty ppt. (except morphine, which is only ppt. from strong solns. of its acetate).

The particular alkaloid must be identified by special tests.

Cinchona bases.

Quinine, $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_8 \cdot 3\text{H}_2\text{O}$, m.p. 177° (anhyd.). Chief salts are sulphate $(\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_8)_2\text{H}_2\text{SO}_4 \cdot 8\text{H}_2\text{O}$ and chloride $(\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_8) \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$.

- (i.) Dilute sols. of sulphate show fluorescence.
- (ii.) Dissolve 0.01 gram of quinine salt in 10 c.c. water, add Cl water and then NH_4OH ; a fine emerald green colour produced which changes to red-brown on adding $\text{K}_3\text{FeC}_6\text{N}_6$ soln. (Thalloquinone reaction).

Cinchonine, $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}$, m.p. 250° .

The thalloquinone reaction gives a white ppt.

Opium bases.

Morphine, $\text{C}_{17}\text{H}_{19}\text{NO}_3 \cdot \text{H}_2\text{O}$. Chief salt the hydrochloride $\text{C}_{17}\text{H}_{19}\text{NO}_3 \cdot \text{HCl} \cdot 4\text{H}_2\text{O}$, silky needle.

- (i.) FeCl_3 gives a dark-blue colour to sols. of morphine salts; the acetate, however, gives a blood-red coloration.
- (ii.) Moisten a crystal on a piece of porcelain with conc. H_2SO_4 and rub a crystal of $\text{K}_2\text{Cr}_2\text{O}_7$ in it; a brown coloration obtained.

Narcotine, $\text{C}_{22}\text{H}_{25}\text{NO}_7$, m.p. 176° .

- (i.) Evaporate a few drops of a soln. in dil. H_2SO_4 to dryness; a fine red residue is left.
- (ii.) Treat a crystal with a few drops of conc. H_2SO_4 , gradually produces a raspberry red colour.

Strychnos bases.Strychnine, $C_{21}H_{22}N_2O_2$, m.p. 284° .

- (i.) Moisten a crystal on a piece of porcelain with conc. H_2SO_4 and rub a crystal of $K_2Cr_2O_7$ in it; a beautiful blue changing to violet and red obtained.
- (ii.) $FeCl_3$ soln. gives a brownish-green ppt. with sols. of its salts.

Brucine, $C_{28}H_{26}N_2O_6$.

- (i.) Add a few drops of conc. HNO_3 to a crystal; it dissolves with formation of a red colour; on heating it turns yellow and violet on adding $SnCl_2$.
- (ii.) Tested as (i.) for strychnine gives orange colour.

Solanum bases.Atropine, $C_{17}H_{23}NO_3$, m.p. 115° .

- (i.) Add few drops of conc. HNO_3 to a crystal; a reddish-brown colour produced.
- (ii.) $FeCl_3$ to a soln. of its salt give a yellow ppt.

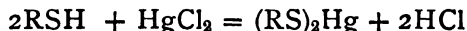
Cocaine, $C_{17}H_{21}NO_4$, m.p. 98° .**XII. CARBON, HYDROGEN, AND SULPHUR PRESENT.**

Mercaptans, Thioethers, and Thiophenes. Each group should be tested for separately.

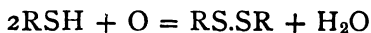
I. MERCAPTANS.

Liquids (higher members solids), with disagreeable odour, mostly insol. in water.

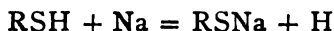
- (i.) Add a few drops of substance to 5 c.c. of an alcoholic solution of $HgCl_2$: a white ppt. of a Hg salt is obtained.



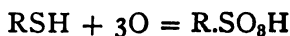
- (ii.) Using $Pb\bar{A}_2$ soln. instead of $HgCl_2$ gives yellow ppt.
- (iii.) Mix 5 c.c. of alcoholic soln. of substance with 2 c.c. conc. NH_4OH , and evaporate to dryness: colourless needles of a disulphide obtained.



- (iv.) Add few drops of substance to soln. of 1 % isatin in H_2SO_4 : a green coloration is produced (fatty).
- (v.) To 1 c.c. of substance add small pieces of Na: H is evolved.



- (vi.) Digest 2 c.c. with conc. HNO_3 under reflux: a sulphonic derivative is obtained, which can be converted into salt and identified.



Methyl mercaptan, CH_3SH , b.p. 20° .

Ethyl mercaptan, $\text{C}_2\text{H}_5\text{SH}$, b.p. 36° . S.G. 0.839 @ 20° .

Mercury mercaptide, $(\text{C}_2\text{H}_5\text{S})_2\text{Hg}$, m.p. 86° . Crys. leaflets almost insol. in water.

Thiophenol, $\text{C}_6\text{H}_5\text{SH}$, b.p. 168° . S.G. 1.078 @ 14° .

Allyl mercaptan, $\text{C}_3\text{H}_7\text{SH}$, b.p. 90° .

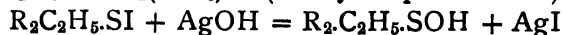
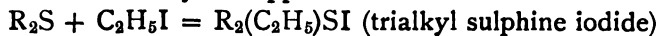
2. THIOETHERS.

Mostly liquids; disagreeable odour; insol. in water, sol. in alcohol and ether (when pure they possess an ethereal odour).

- (i.) Mix 1 c.c. $\text{C}_2\text{H}_5\text{I}$ with 1 c.c. of substance, and warm (if necessary); now add moist Ag_2O and well shake with water, warm, and filter. Test filtrate—

(a) With litmus: alkaline.

(b) With soln. of salt of any heavy metal: oxide or hydrate pptd.



Soluble in H_2O

- (ii.) To soln. of substance in alcohol add soln. of PbO in NaOH : ppt. of Pb salt obtained.
- (iii.) Det. b.p.

Methyl sulphide, $(\text{CH}_3)_2\text{S}$, b.p. 37.5° .

Ethyl sulphide, $(\text{C}_2\text{H}_5)_2\text{S}$, b.p. 91° .

Allyl sulphide, $(\text{C}_3\text{H}_5)_2\text{S}$, b.p. 140° . Colourless oil, with disagreeable smell; chief constituent of oil of garlic.

Phenyl sulphide, $(\text{C}_6\text{H}_5)_2\text{S}$, b.p. 292° . Colourless liquid with odour of leeks.

Ethyl disulphide $(\text{C}_2\text{H}_5)_2\text{S}_2$, b.p. 151° . Oil with odour of garlic.

Vinyl sulphide, $(\text{C}_2\text{H}_3)_2\text{S}$, b.p. 101° . S.G. 0.9125.

3. THIOPHENES.

- (i.) Dissolve crystal of isatin in 2 c.c. cold conc. H_2SO_4 and to this soln. add a few drops of substance: a deep blue coloration produced. (Indophenin reaction.) Given by all Thiophene compounds. Similar colour produced with furfurane $\text{C}_4\text{H}_4\text{O}$, pyrrol $\text{C}_4\text{H}_4\text{N}$, and carbazol $(\text{C}_6\text{H}_4)_2\text{NH}$.
- (ii.) Nitro- and sulphonic acid derivatives may be easily produced, isolated, and identified by m.p. or b.p.
- (iii.) Dissolve 0.1 gram of thiophene in 1 c.c. conc. H_2SO_4 , and add this soln. to a soln. of 0.1 gram of phenanthraquinone in 1 c.c. of glacial acetic acid; a dark - blue-coloured soln. is obtained. (Reaction of Laubenheimer.) This colour is produced by all dicarbonyl compounds CO.CO , viz. benzil, alloxan, etc.

Thiophene, $\text{C}_4\text{H}_4\text{S}$, b.p. 84° . S.G. 1.062 @ 23° .

Nitrothiophene, $\text{C}_4\text{H}_3(\text{NO}_2)\text{S}$, m.p. 44° . Bright yellow prisms.

Dinitrothiophene, $\text{C}_4\text{H}_2(\text{NO}_2)_2\text{S}$, m.p. 52° . Sol. in alcoholic KOH to dark red soln.

α Thiotolene, $\text{C}_4\text{H}_3.\text{S}.\text{CH}_3$, b.p. 126° .

β " " " b.p. 113° .

Dimethyl Thiophenes, $\text{C}_4\text{H}_2\text{S}(\text{CH}_3)_2$.

(i.) 1.3, b.p. 137° – 138° . Isatin reaction gives emerald-green coloration.

(ii.) 1.4, b.p. 135° . Isatin reaction gives cherry-red coloration.

XIII. CARBON, HYDROGEN, SULPHUR, AND OXYGEN PRESENT.

Sulphonic acids (or their salts) and alkyl sulphates (or their salts). [Aldehyde and Ketone Bisulphites.]

- (i.) Digest 2 grams of substance with 50 c.c. of water under reflux. Distil two-thirds, and test distillate for alcohol. Residue in flask test for sulphuric acid. Body can be identified by separating alcohol and determining its b.p.; this reaction given by an alkyl sulphate.
- (ii.) Fuse 1 gram of substance with 2 grams solid KOH in a nickel (or porcelain) crucible to 200° C. Cool, dissolve in water, acidify with HCl, when a phenol or an alcohol will be liberated and may be separated by extraction with ether (or if insol. in water, filtered off). The phenol or alcohol can be identified by usual tests; this reaction given by a sulphonic acid or salt. To confirm the sulphonic compound—
 - (a) Mix 1 gram of substance with 2 grams PCl_5 , and heat on water-bath till action over; pour into water, when oil settles out, which extract with ether, etc. = $\text{R.SO}_2\text{Cl}$. Det. b.p.
 - (b) Mix 1 gram of oil obtained in (a) with 2 grams $(\text{NH}_4)_2\text{CO}_3$, and heat on water-bath till smell of chloride gone. Treat with water and filter: residue is a sulphonamide, which can be recrystallized from alcohol, and m.p. determined.

- A. Methyl sulphuric acid, CH_3HSO_4 . A thick oil; chief salts are—
- (i.) $\text{CH}_3\text{SO}_4\text{K}$. Deliquescent solid.
 - (ii.) $(\text{CH}_3\text{SO}_4)_2\text{Ba} \cdot 2\text{H}_2\text{O}$. Crys. plates.

Ethyl sulphuric acid, $C_2H_5.HSO_4$. Thick liquid ; chief salts are—

(i.) $C_2H_5.SO_4.K$. Crys. plates.

(ii.) $(C_2H_5.SO_4)_2Ba.2H_2O$. Large crys. tablets.

Amyl sulphuric acid, $C_5H_{11}.HSO_4$. A thick non-crystallizable liquid. S.G. 1.316 @ 16°.

(i.) $C_5H_{11}.SO_4.K$. Crys. in plates.

(ii.) $(C_5H_{11}.SO_4)_2Ba.2H_2O$. Crys. in large tablets.

B. Methyl sulphonic acid, $CH_3.SO_3H$. Thick liquid.

(i.) $(CH_3.SO_3)_2Ba.1\frac{1}{2}H_2O$.

(ii.) $CH_3.SO_3Cl$, b.p. 160°.

Ethyl sulphonic acid, $C_2H_5.SO_3H$. Thick liquid.

(i.) $(C_2H_5.SO_3)_2Pb$. Crys. leaflets.

(ii.) $C_2H_5.SO_3Cl$, b.p. 177°.

Benzene sulphonic acid, $C_6H_5.SO_3H$, m.p. 50°.

(i.) $(C_6H_5.SO_3)_2Ba.H_2O$. Pearly leaflets.

(ii.) $C_6H_5.SO_3Cl$, b.p. 116°. S.G. 1.378 @ 23°.

(iii.) $C_6H_5.SO_3NH_2$, m.p. 150°.

o-Toluene sulphonic acid, $C_6H_4<\begin{smallmatrix} CH_3 \\ SO_3H \end{smallmatrix} \begin{smallmatrix} (1) \\ (2) \end{smallmatrix}$
Liquid ; its sulphamide, m.p. 155°.

m-Toluene sulphonic acid, $C_6H_4<\begin{smallmatrix} CH_3 \\ SO_3H \end{smallmatrix} \begin{smallmatrix} (1) \\ (3) \end{smallmatrix}$
Liquid ; its sulphamide, m.p. 107°.

p-Toluene sulphonic acid, $C_6H_4<\begin{smallmatrix} CH_3 \\ SO_3H \end{smallmatrix} \begin{smallmatrix} (1) \\ (4) \end{smallmatrix}$
Liquid ; its sulphamide, m.p. 137°.
its chlorsulphonic acid, m.p. 69°.

Naphthalene α sulphonic acid, $C_{10}H_7.SO_3H$. Crystalline, deliquescent.

Naphthalene β sulphonic acid, $C_{10}H_7.SO_3H$. Non-deliquescent scales.

(iii.) Test specially for aldehydes and ketones ; they are best separated from their bisulphite derivatives by heating with Na_2CO_3 soln.

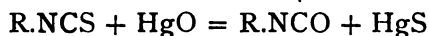
XIV. CARBON, HYDROGEN, SULPHUR, AND NITROGEN PRESENT.

Mustard Oils (Isothiocyanates), Thiocyanates, Thioureas.
Test specially for each class, viz.—

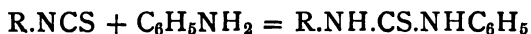
I. MUSTARD OILS.

Colourless liquids (some solids) with characteristic penetrating odours, almost insol. in water.

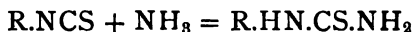
- (i.) Heat 0.5 c.c. substance with 0.5 gram of yellow HgO: black ppt. of HgS with evolution of disagreeable odour of an Isocyanate.



- (ii.) Warm 0.5 c.c. substance with 0.5 c.c. aniline; cool and allow to crystallize: a thiourea formed, which may be identified by m.p.



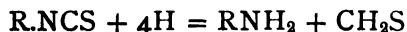
- (iii.) Use conc. NH_4OH instead of aniline.



- (iv.) Heat 2 grams of substance with 10 c.c. absolute alcohol under reflux till odour of oil gone; pour into water and re-crystallize solid that settles out from alcohol. Determine m.p.



- (v.) Mix 1 c.c. with 10 c.c. HCl and Zn dust: substance reduced to an amine and CH_2S (thioformaldehyde)—the latter body has odour of onions. The amine can be separated and identified by usual tests.



- (vi.) Heated with conc. HCl under reflux, CO_2 and SH_2 are evolved, which may be detected.

H

Methyl mustard oil, CH_3NCS , m. p. 34° , b.p. 119° .

Ethyl mustard oil, $\text{C}_2\text{H}_5\text{NCS}$, b.p. 133° .

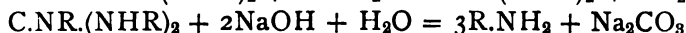
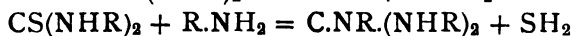
Allyl mustard oil, $\text{C}_3\text{H}_5\text{N}:\text{CS}$, b.p. 150.7° . S.G. $1.017 @ 10^\circ$.

Phenyl mustard oil, $\text{C}_6\text{H}_5\text{N}:\text{CS}$, b.p. 222° (phenyl thiourethane, m.p. 71°).

2. THIOUREAS.

Heat 2 grams with 10 c.c. conc. HCl under reflux ; distil two-thirds of liquid, and examine as follows :—

- (a) Distillate—contains a mustard oil, which may be detected as in XIV. 1.
- (b) Residue—contains a guanidine derivative. Heat with strong NaOH under reflux, when an amine and CO_2 produced may be identified.



Thiourea, $\text{CS}(\text{NH}_2)_2$, m.p. 169° . Crys. solid ; easily sol. in water and alcohol, difficultly sol. in ether. Hydrolysis with acids or alkalies yields $\text{CO}_2 + \text{NH}_3 + \text{H}_2\text{S}$.

Ethyl thiourea, $\text{CS} \begin{smallmatrix} \text{HNC}_2\text{H}_5 \\ \text{NH}_2 \end{smallmatrix}$, m.p. 106° .

Diethyl thiourea, $\text{CS}(\text{NH.C}_2\text{H}_5)_2$, m.p. 77° .

Allyl thiourea, $\text{CS} \begin{smallmatrix} \text{NH.C}_3\text{H}_5 \\ \text{NH}_2 \end{smallmatrix}$, m.p. 74° .

Phenyl thiourea, $\text{CS} \begin{smallmatrix} \text{NHC}_6\text{H}_5 \\ \text{NH}_2 \end{smallmatrix}$, m.p. 154° .

Diphenyl thiourea, $\text{CS}(\text{NH.C}_6\text{H}_5)_2$, m.p. 141° .

3. THIOCYANATES (metallic and alkyl).

- (i.) Mix 1 c.c. with 5 c.c. HCl and Zn dust : reduced to HCN (evolved), mercaptan, and other products.
- (ii.) Heat with conc. HCl under reflux : converted into thioether, CO_2 and NH_3 . All these products can be identified.

- (iii.) Oxidized when heated with conc. HNO_3 to sulphonic acids, etc.

A. Metallic Derivatives. All insol. in water excepting those of the alkalies.

- (i.) FeCl_3 soln. produces a dark red coloration with soln. of thiocyanic acid and its soluble salts ; not discharged by HCl , but discharged by nascent H (Zn and H_2SO_4) or HgCl_2 soln.
- (ii.) CuSO_4 soln. to conc. solns. gives a black ppt. of $\text{Cu}(\text{SCN})_2$, which turns white on standing or on adding FeSO_4 , owing to formation of CuSCN .

Ammonium Thiocyanate, CN.S.NH_4 , m.p. 174° .

- (1) FeCl_3 give a deep red coloration to soln. of CN.S.NH_4 .
- (2) HgCl_2 ppt. a gray amorphous powder of $(\text{CN.S})_2\text{Hg}$ (Pharaoh's serpents).

B. Alkyl Derivatives.

Liquids having a leek-like odour and insol. in water ; react as 3 (i.), (ii.), (iii.).

Methyl thiocyanic ester, $\text{CH}_3\text{S.CN}$, b.p. 133° . S.G. $1.088 @ 0^\circ$.

Ethyl thiocyanic ester, $\text{C}_2\text{H}_5\text{SCN}$, b.p. 142° . S.G. $1.033 @ 0^\circ$.

Phenyl thiocyanic ester, $\text{C}_6\text{H}_5\text{SCN}$, b.p. 131° .

Isopropyl thiocyanic ester, $\text{C}_3\text{H}_7\text{S.CN}$, b.p. 152° .

Allyl thiocyanic ester, $\text{C}_3\text{H}_5\text{S.CN}$, b.p. 161° . S.G. $1.071 @ 0^\circ$.

XV. CARBON, HYDROGEN, SULPHUR, OXYGEN, AND NITROGEN OR HALOGEN PRESENT.

A. Amino-sulphonic acids (*e.g.* sulphanilic acid) ; sulphonamides.

B. Chloro-sulphonic acids.

Test for each class specially.

1. AMINO-SULPHONIC ACIDS.

Diazotize the compound and couple with either dimethyl aniline or α or β naphthol: azo dyes will be produced, viz.—

Sulphanilic acid and dimethyl aniline yield methyl orange.

Sulphanilic acid and α naphthol yield orange I.

” ” and β ” ” orange II.

Metanilic acid and diphenylamine yield metanilic yellow.

To diazotize the amino-sulphonic acids, take about 0.2 gram of substance in a test-tube, and dissolve it in dilute Na_2CO_3 soln.; to this add 1 c.c. of saturated NaNO_2 soln.; well cool, and add dil. HCl till free HNO_2 is present (KI and starch paper test).

To couple with naphthol, dissolve 0.1 gram naphthol in NaOH soln., and add the soln. so obtained to the diazotized soln., and, if necessary, make alkaline.

To couple with dimethyl aniline, dissolve 0.2 c.c. of it in dil. HCl till just acid (use fuchsine paper, which is decolorized by free HCl), and add soln. so obtained to the diazotized soln., and make strongly alkaline.

Sulphanilic acid, $\text{C}_6\text{H}_4\text{<}\begin{smallmatrix} \text{NH}_2 & (1) \\ \text{SO}_3\text{H} & (4) \end{smallmatrix}$. Crystallizes from hot water with 1 mol H_2O .

(1) Yields quinone readily with MnO_2 and H_2SO_4 .

(2) Yields aniline when fused with KOH .

Metanilic acid, $\text{C}_6\text{H}_3\text{<}\begin{smallmatrix} \text{NH}_2 & (1) \\ \text{SO}_3\text{H} & (3) \end{smallmatrix}$. Crys. solid; easily sol. in hot water, insol. alcohol and ether; decomposed on heating.

Disulphanilic acid, $\text{C}_6\text{H}_3\cdot\text{NH}_2\cdot(\text{SO}_3\text{H})_2\cdot(1.2.4)$. Red crys.; very sol. in alcohol and ether.

1.4 Naphthylamine sulphonic acid or naphthionic acid, $\text{C}_{10}\text{H}_6(\text{NH}_2)\text{SO}_3\text{H}$. Crys. solid; sparingly sol. in water.

(i.) Produces congo red with diazotized benzidine.

(ii.) Dilute solns. of its salts show violet fluorescence.

2.6 Naphthylamine sulphonic acid, $\text{C}_{10}\text{H}_6(\text{NH}_2)\text{SO}_3\text{H}$ (Brönner's acid). Crys. solid; sol. in warm water

(i.) Solution shows blue fluorescence.

(ii.) Yields brownish-yellow to brownish-red dyes with diazotized bases.

2.7 Naphthylamine sulphonic acid, $C_{10}H_6(HN_2)SO_3H$
(Bayer's acid). Silky needles; insol. in cold water.

2. SULPHONAMIDES.

- (i.) Dissolve in alkalis, producing salts, *e.g.* $R.SO_2NHK$.
- (ii.) Alcoholic solns. give a ppt. with $AgNO_3$ of $R.SO_2NHAg$.
- (iii.) Treated with C_6H_5COCl and $NaOH$ yield acid derivatives, *viz.* $R.SO_2NH.C_6H_5CO$.
- (iv.) Fused with $NaOH$ phenols are obtained, NH_3 evolved, etc.

Saccharin is the anhydride of o-sulphamin-benzoic acid,
viz. $C_9H_4 \cdot \overset{CO}{SO_2} \cdot NH$.

- (i.) Heated with HCl under reflux converts it to o-sulphobenzoic acid and NH_4Cl ; these can be tested for.
- (ii.) Fused with solid $NaOH$ at $230^\circ C$., cooled, dissolved in water, and acidified with HCl , when salicylic acid separates, and may be identified by usual tests.

3. CHLORO-SULPHONIC ACIDS. These may be identified as in XIII. (ii.) (*b*).

Methyl sulphonic chloride, $CH_3.SO_2Cl$, b.p. 160° .

Ethyl sulphonic chloride, $C_2H_5.SO_2Cl$, b.p. 173° .

Benzene sulphonic chloride, $C_6H_5SO_2Cl$, b.p. 247° .

o-Toluene sulphonic chloride, $C_6H_4.CH_3.SO_2Cl$ (1.2). Oil.

m-Toluene sulphonic chloride, $C_6H_4.CH_3.SO_2Cl$ (1.3). Oil.

p-Toluene sulphonic chloride, $C_6H_4.CH_3.SO_2Cl$ (1.4), m.p. 69° .

Benzene m. disulphonic chloride, $C_6H_4(SO_2Cl)_2$ (1.3), m.p. 63° .

Naphthalene α Sulphonic chloride, $C_{10}H_7.SO_2Cl$, m.p. 56° .

 " β " " m.p. 76° .

XVI. SPECIAL REACTIONS.

1. The following para derivatives, when oxidized by dil. chromic acid in water or acetic acid, are oxidized to

quinone, which can be identified by odour, volatility in steam, and m.p. 116°C .

Phenylene-diamine, amidophenol, phenol sulphonic acid, sulphanilic acid, hydroquinone, amido-azobenzene, diamidodiphenyl, etc.

2. The following yield α naphthoquinone when oxidized as above, m.p. 125°C . :—

(i.) α amido-naphthol, α naphthylamine, nitro- α -naphthol, (1.4) diamidonaphthalene, α (1.4) dioxynaphthalene.

(ii.) Naphthalene, CrO_3 in glacial acetic acid.

3. The following yield anthraquinone, m.p. 277° .

Anthracene and dibromanthracene.

Quinone. Yellow crys., pungent odour; m.p. 160° ;

reduced to $\text{C}_6\text{H}_4(\text{OH})_2$ by SO_2 .

Anthraquinone. Heat 0.1 gram of substance with Zn dust and 5 c.c. NaOH soln.: a deep blood-red soln. of oxanthrol is produced.

α Naphthaquinone.

(i.) Heat 0.1 gram with dil. H_2SO_4 (5 to 1): gives violet coloration due to a condensation product.

(ii.) Heat 0.1 gram with KOH soln.: reddish-brown soln. Add dil. HCl: a bright red ppt.

SOLUBILITY OF ORGANIC SUBSTANCES IN WATER

- I. C AND H. All insoluble except the lowest members of the aliphatic series. Soluble in C_2H_5OH .
- II. C, H, AND HALOGEN. All insoluble ($CHCl_3$, CHI_3 slightly soluble). Readily soluble in C_2H_5OH , $(C_2H_5)_2O$, CS_2 , and $CHCl_3$. Alkyl chlorides are lighter than water, the iodides heavier.
- III. C, H, AND O.
1. ALCOHOLS.
- (i.) Aliphatic.
- (a) Monohydric. Lower members soluble ($C_5H_{11}OH$ requires 40 parts of water).
- (b) Dihydric. More soluble than monohydric.
- (c) Trihydric. More soluble still; solubility increases with accumulation of OH groups.
- (ii.) Aromatic. Less soluble than aliphatic.
- Solutions produced are neutral.
- Solubility in ether decreases with accumulation of OH groups.
2. PHENOLS.
- (i.) Monohydric. Lower members soluble; easily soluble in $NaOH$. Soluble in C_2H_5OH and $(C_2H_5)_2O$.
- (ii.) Dihydric. More soluble; also soluble in Na_2CO_3 soln.
- (iii.) Trihydric. Ditto.

3. ALDEHYDES.

- (i.) Aliphatic. Lower members soluble ; bisulphite derivatives slightly soluble ; ammonia derivatives soluble.
- (ii.) Aromatic. All insoluble.

4. KETONES.

- (i.) Aliphatic. Acetone miscible with water in all proportions ; others mostly insoluble.
- (ii.) Aromatic. Mostly insoluble.

5. QUINONES. Insoluble ; characteristic odour and volatile in steam. Soluble in C_2H_5OH and $(C_2H_5)_2O$.

6. ETHERS. Less soluble than corresponding alcohols. Solutions neutral.

7. ACIDS.

- (i.) Aliphatic. Monobasic.

(a) Formic, acetic, propionic, butyric mix in all proportions.

(b) Isobutyric sol. in 3 pts. water.

(c) Higher members less and less soluble.

Dibasic. Mostly soluble, and solubility increases with accumulation of $COOH$ groups.

Hydroxy. Generally more soluble than corresponding acid.

- (ii.) Aromatic. Less soluble than aliphatic ; easily sol. in ether. All acids are easily soluble in $NaOH$ soln. or Na_2CO_3 soln.

Aromatic oxyacids are easily sol. in $CHCl_3$.

Most aromatic acids sublime undecomposed.

8. ACID ANHYDRIDES. Combine with water to produce acid, and hence dissolve if corresponding acid is soluble. Combination is slow in the cold, quicker on heating ; higher members require long heating.

9. CARBOHYDRATES. Easily soluble in water except starch and cellulose ; solution neutral.
- (a) Glucoses. Sparingly sol. in abs. C_2H_5OH ; insol. in ether.
 - (b) Saccharoses. Ditto.
 - (c) Polysaccharrides. Ditto.
10. GLUCOSIDES. Following are more or less soluble :
Salicin, populin, helicin, myronic acid, tannins (certain), arbutin.
11. ESTERS. Insoluble (decomposed on warming and give acid reaction). Methyl oxalate $(CO.OCH_3)_2$ easily sol. in water to an acid solution.

IV. C, H, AND N.

1. AMINES.

A. Monamines.

- (i.) Aliphatic. Lower members soluble and soln. alkaline ; salts easily soluble. HCl salts soluble in abs. C_2H_5OH .
- (ii.) Aromatic.
Less soluble than aliphatic.

All primary are soluble in acids ; secondary and tertiary are not.

B. Diamines. Soluble in water, alcohol, and ether ; salts also soluble.

- 2. CYANIDES. All insoluble (CH_3CN and C_2H_5CN slightly soluble).
- 3. ISOCYANIDES. All insoluble (easily soluble in alcohol and ether).
- 4. HYDRAZINES. Sparingly soluble ; salts easily soluble (note $C_6H_5NHNH_2$).
- 5. ALKALOIDS. Insoluble ; easily soluble in acids, hence salts soluble.

V. C, H, O, AND HALOGEN.

1. ACID CHLORIDES. Decomposed by water, evolving HCl, and soluble if corresponding acid is soluble. Note aromatic only slowly acted upon.
2. SUBSTITUTED ACIDS. More soluble than corresponding acid. Solution acid. No HCl evolved.
3. CHORAL AND CHORAL HYDRATE. Soluble in water. Chloral, a liquid; solidifies on adding a little water to it.

VI. C, H, O, AND N.

1. AMIDES. Lower members of aliphatic soluble, all others insoluble. $\text{C}_6\text{H}_5\text{CO.NH}_2$ sol. in hot water.
2. AMINO ACIDS. Soluble in water; solutions neutral; insoluble as a rule in $\text{C}_2\text{H}_5\text{OH}$ and $(\text{C}_2\text{H}_5)_2\text{O}$.
3. ANILIDES. Sparingly soluble in cold water, more soluble in hot.
4. NITRO-COMPOUNDS.
 - (i.) All nitro-hydrocarbons insoluble.
 - (ii.) Nitrophenols, slightly soluble; salts easily soluble to yellow or red solutions.
 - (iii.) Nitranilines, more or less soluble (some give coloured solns.).
 - (iv.) Nitro acids, sparingly soluble.
 - (v.) Nitro-aldehydes, more or less soluble.
5. AZO-COMPOUNDS.
 - (i.) Free azo-compound usually insoluble.
 - (ii.) Salts with acids or alkalies usually soluble (dyes).
6. UREAS.
 - (i.) Urea very soluble.
 - (ii.) Alkyl areas more or less soluble.
7. UREIDES.
 - (i.) Mostly soluble in water.

(ii.) Note following :—

Oxalyl urea or parabanic acid, $\text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH} \cdot \text{CO}$.

Oxaluric acid, $\text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{CO}_2\text{H}$.
 NH_2 .

Malonyl urea or barbituric acid, $\text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_2$.

Mesoxalyl urea or alloxan, $\text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{CO}$.

(iii.) Uric acid, difficultly soluble, easily soluble in NaOH ;
 insol. in alcohol and ether.

The following bodies are allied to uric acid :—

Guanine, $\text{C}_5\text{H}_5\text{N}_5\text{O}$, insoluble.

Xanthine, $\text{C}_5\text{H}_4\text{N}_4\text{O}_2$, soluble in boiling water.

Theobromine, $\text{C}_5\text{H}_2(\text{CH}_3)_2\text{N}_4\text{O}_2$, difficultly soluble in hot
 water.

Caffeine, $\text{C}_8\text{H}(\text{CH}_2)_3\text{N}_4\text{O}_2$, difficultly soluble in cold
 water.

8. CYANATES.

(i.) Alkaline salts soluble.

(ii.) Cyanuric acid, sparingly soluble.

(iii.) Esters, insoluble.

9. OXIMES. Sparingly soluble in water (acetoxime easily
 soluble).

10. HYDRAZONES. Very sparingly soluble in water ; mostly
 coloured compounds (those of hexoses are colourless) ;
 soluble in alcohol.

11. OSAZONES. Yellow solids ; mostly insol. in water ; dif-
 ficultly soluble in alcohol. Soluble in $\text{C}_6\text{H}_5\text{NH}_2$, from
 which they crystallize well.

12. ESTERS OF NITRIC AND NITROUS ACID. Insoluble.

13. ALKALOIDS. Insoluble (almost) ; easily soluble in acids,
 hence salts soluble.

VII. C, H, AND S.

1. MERCAPTANS. Insoluble in water. Sol. in C_2H_5OH and $(C_2H_5)_2O$. K and Na derivatives sol. in water ; all others insoluble. Disagreeable, penetrating odour.
2. THIOETHERS. Insoluble in water.
3. THIOPHENES. Insoluble in water.

VIII. C, H, S, AND N.

1. THIOUREAS.
 - (i.) Thiourea easily soluble.
 - (ii.) Substituted more or less soluble.
2. MUSTARD OILS. Insoluble. Characteristic penetrating odour.
3. THIOCYANATES.
 - (i.) Acid and the alkaline salts soluble.
 - (ii.) Esters insoluble. Leek-like odour.

IX. C, H, S, AND O.

1. Sulphonic Acids. Soluble ; also their salts.
2. Alkyl Sulphates. Soluble ; also their salts.
3. Sulphones. Insoluble.
4. Aldehyde and ketone bisulphites. Very slightly soluble.

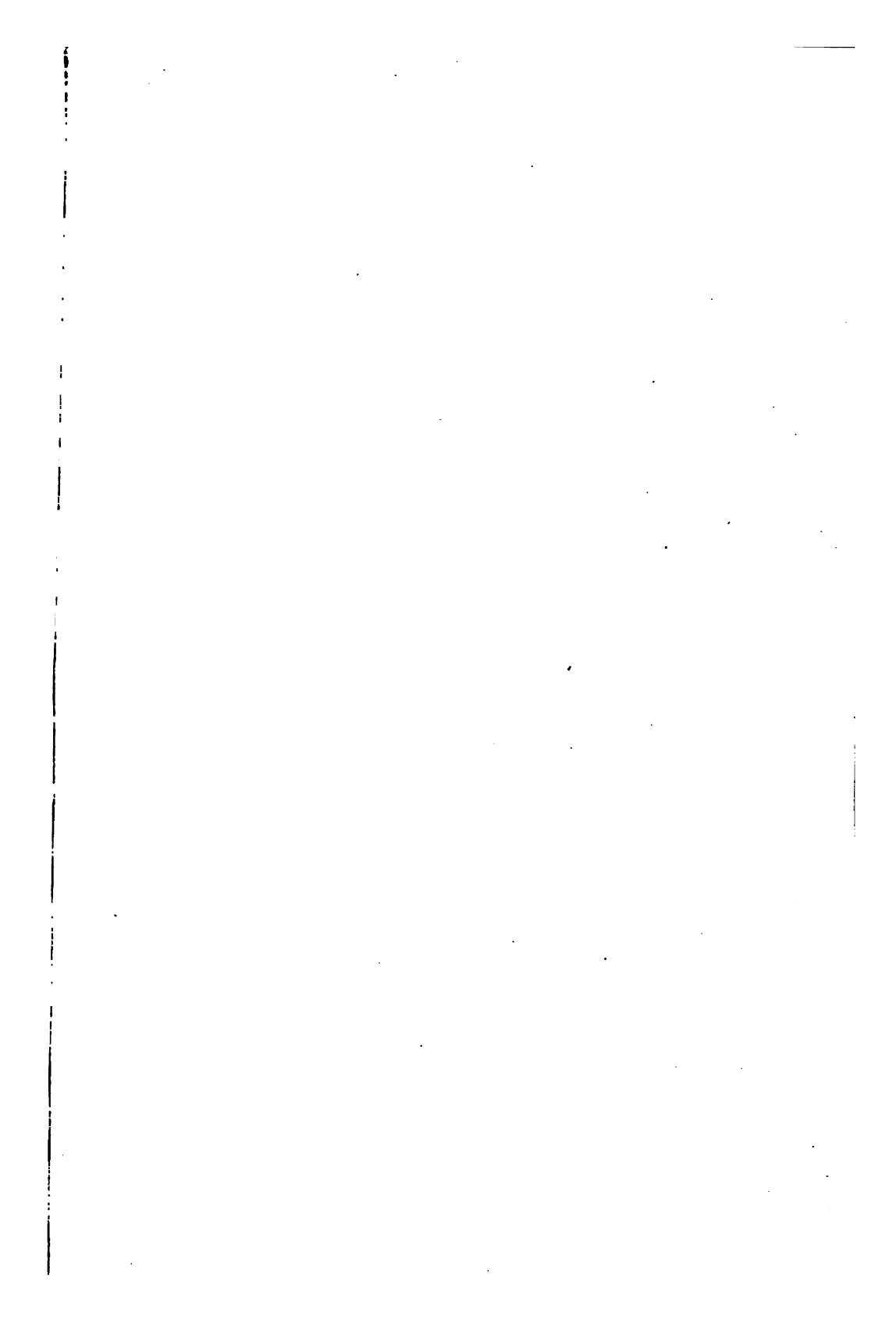
X. C, H, S, O, AND N.

1. AMINO-SULPHONIC ACIDS. Sparingly soluble (*e.g.* sulphanic acid).
2. SULPHAMIDES. Insoluble (note saccharin very soluble).
3. NITROSULPHONIC ACIDS. Soluble.

XI. C, H, S, O, AND Cl.

1. Chlorosulphonic acids. Slightly soluble.
2. Sulphonic Chloranhydrides. Insoluble ; converted into sulphonic acids on boiling.

THE END.



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